Scheme 1. Preparation of acyclic arrays

Scheme 3. Novel gamma sulfenylation and diene transposition.

 $\beta$  37 R =TBS; Z = O

Scheme 4. Prepartion of stereopentad progenitors. 1.1 n-BuLi (2.2 eq), THF, -78°C to -7°C, 1.2 MeI (5 eq), -90°C to -50°C; 2 m-CPBA (2.2 eq);  $\mathrm{CH_2Cl_2}$ , 25°C, 30 min; 3 TBSOTf (1.2 eq), Lutidine (2 eq).  $CH_2CI_2$ , 25°C, 2h; 4.1 n-BuLi (2.2eq), THF, -78°C to -5°C, 90 min; 4.2 Eschenmoser's salt (2.5 eq), THF, -70°C to 0°C, 1.5 h; 5 m-CPBA (4 eq); CH2Cl2, 25°C, 1h; 6 TBHP + 5% Mo(CO)<sub>6</sub>, 88% >15:1  $\alpha/\beta$ ; 7 10% (R,R)-Mn(salen)C1, H<sub>2</sub>O<sub>2</sub>, 1eq  $NH_4OAc$ , 83% 1:>20  $\alpha/\beta$  , 8  $OsO_4$ cat. >80%, single diastereomer

OH 
$$\frac{31}{31}$$
 cat. >80%, single diaster  $\frac{29}{2}$  cat. >80%, single diaster  $\frac{29}$ 

MeOH-benzene, 0°C, 1.5 h, 85%

44

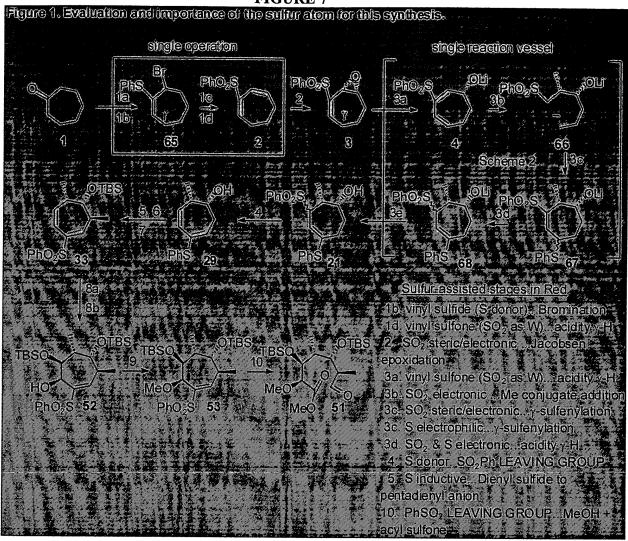
PhO<sub>2</sub>S 
$$OR^1$$
  $OR^2$   $OMe$   $OTBS$   $OTBS$ 

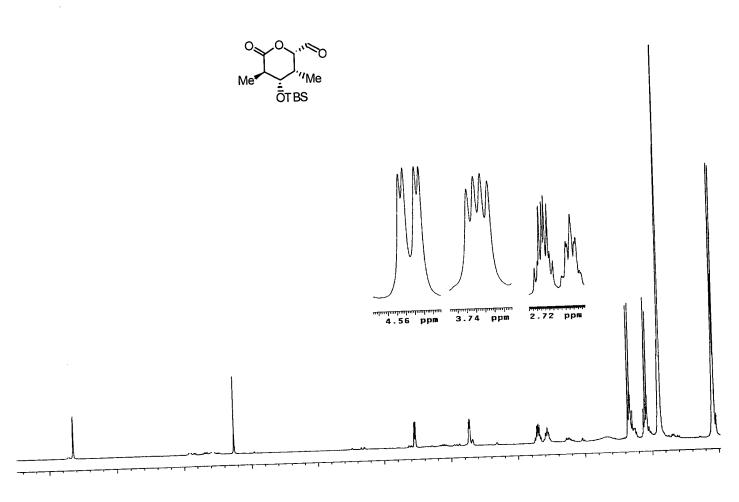
# Scheme 6. Synthesis of the ent-C15-C21 fragment of Concanamycin F.

a TBSOTf, 2,6-Lutidine, CH<sub>2</sub>Cl<sub>2</sub>, -78°C, 24h, 99%; b KOH/Mel/DMSO, 25°C, 5 min; 94%; c O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, MeOH (1:2), NaHCO<sub>3</sub>, -78°C, 5 min, then PPh<sub>3</sub>, 92%

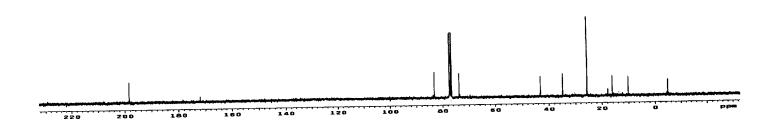
C1-C7 of Discodermolide

Apoptolidin and C1-C7 of Discodermolide. a BH<sub>3</sub>·THF (1.6 eq), THF, 0°C, warm to 25°C, 12 h; b 1.5 eq DIBAL-H, -78°C; c  $O_3$ , CH<sub>2</sub>CI<sub>2</sub>/MeOH (1:2), NaHCO<sub>3</sub>, -78°C, 5 min; d Ag<sub>2</sub>O, MeI, CH<sub>3</sub>CN, reflux, 3h; e PDC (5 eq), CH<sub>2</sub>CI<sub>2</sub>, 25°C, 10 h

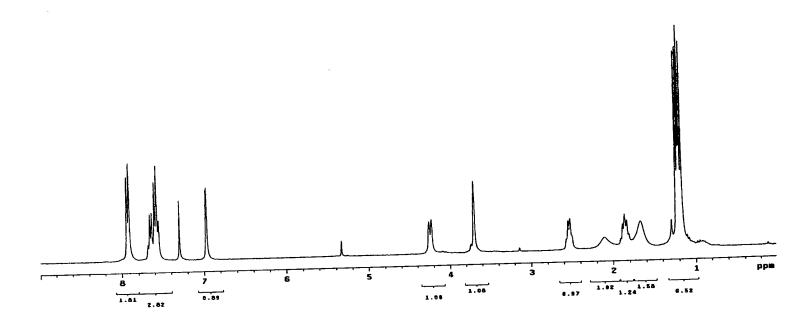




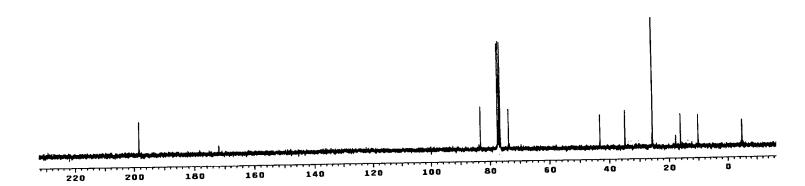
300 MHz <sup>1</sup>H NMR of compound 22 in CDCl<sub>3</sub>



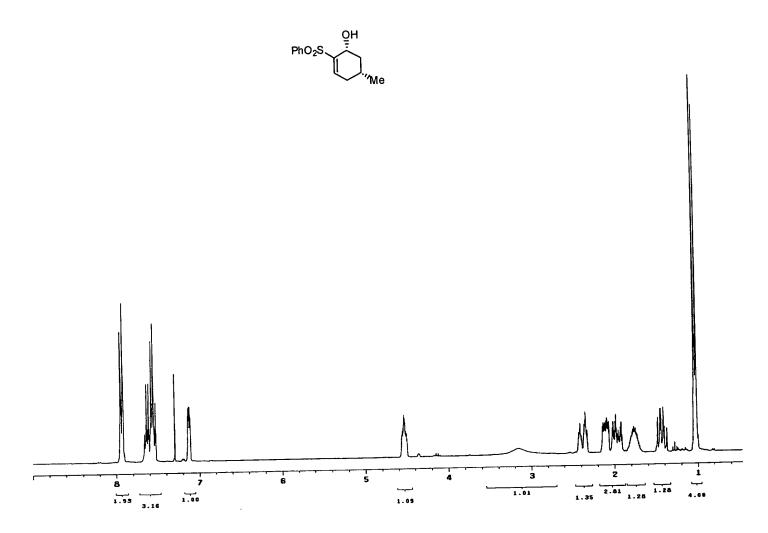
75MHz  $^{13}$ C NMR of compound 22 in CDCl $_3$ 



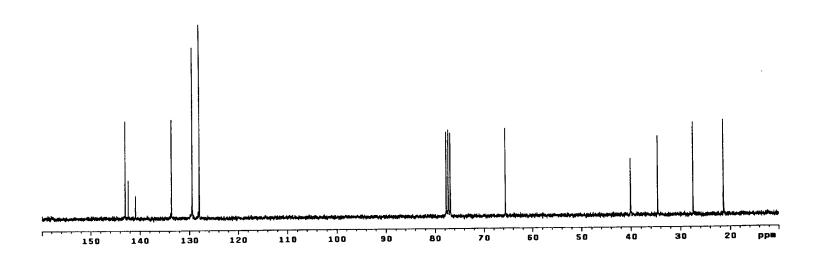
300MHz <sup>1</sup>H NMR of compound **23** in CDCl<sub>3</sub>



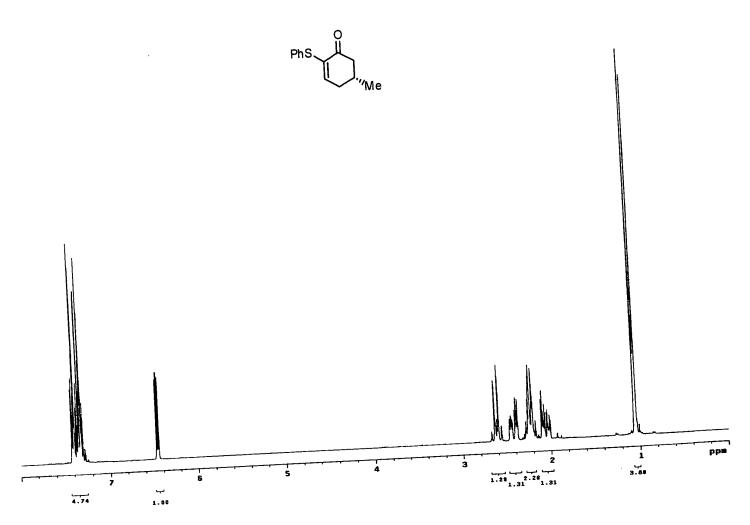
75MHz  $^{13}$ C NMR of compound 23 in CDCl $_3$ 



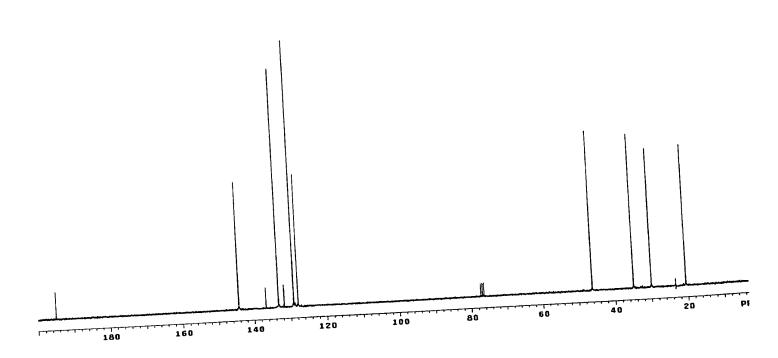
300MHz <sup>1</sup>H NMR of compound **24** in CDCl<sub>3</sub>



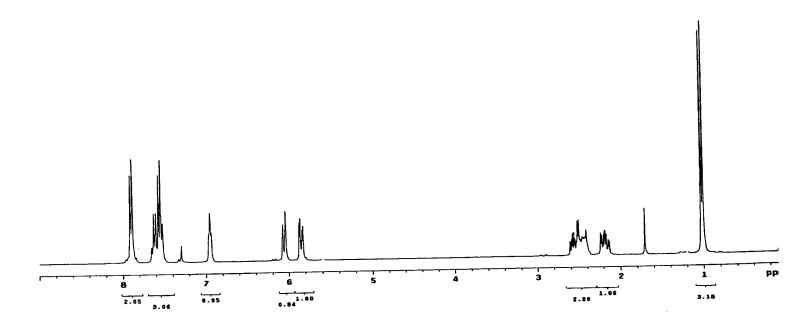
75MHz  $^{13}$ C NMR of compound **24** in CDCl<sub>3</sub>



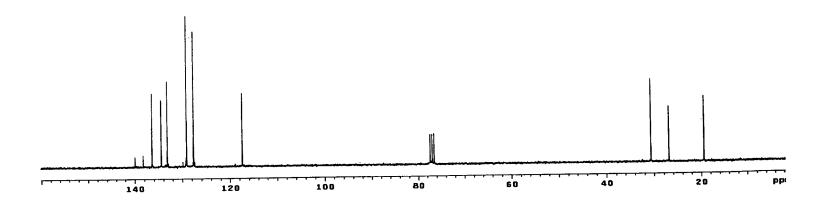
300MHz  $^1\text{H}$  NMR of compound 28 in CDCl $_3$ 



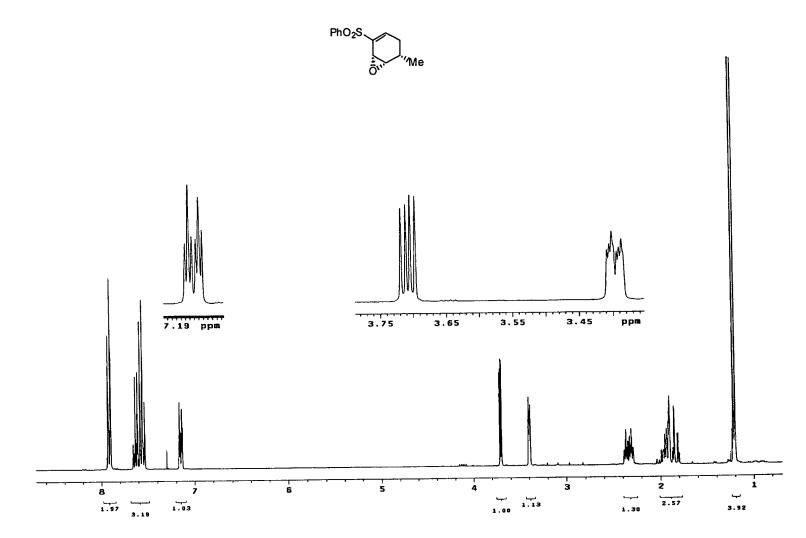
75MHz  $^{13}$ C NMR of compound 28 in CDCl $_3$ 



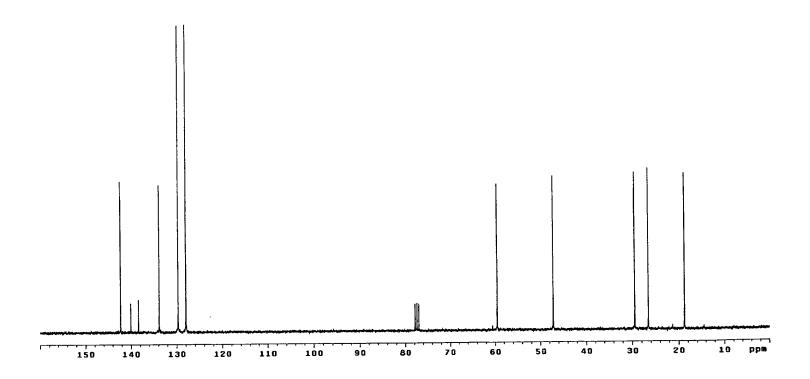
300MHz <sup>1</sup>H NMR of compound **29** in CDCl<sub>3</sub>



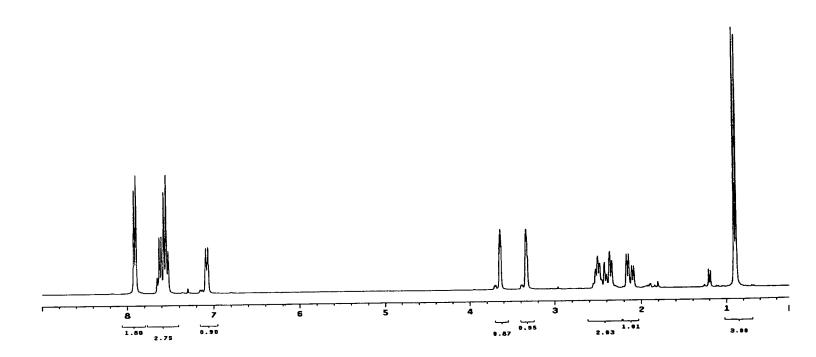
75MHz  $^{13}$ C NMR of compound **29** in CDCl<sub>3</sub>



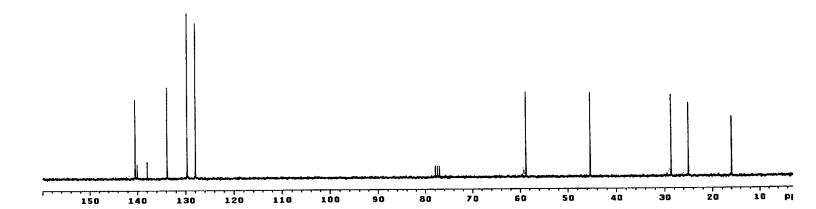
300MHz  $^1\mathrm{H}$  NMR of compound 30 in CDCl $_3$ 



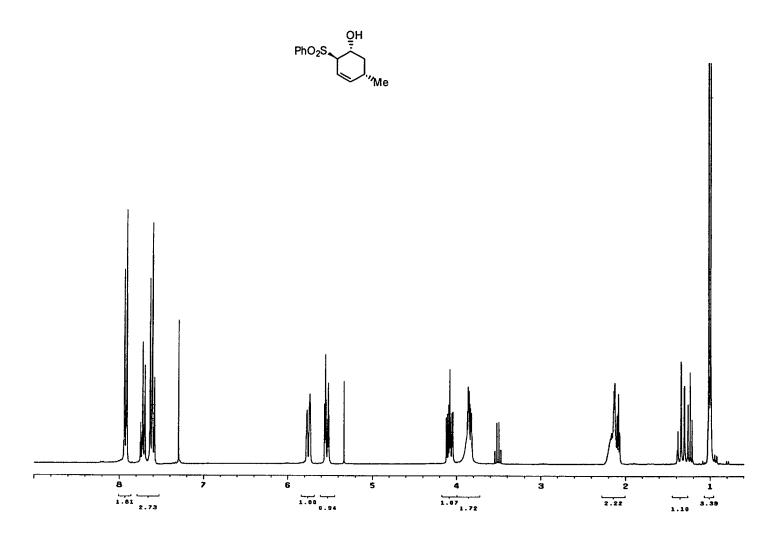
75MHz  $^{13}$ C NMR of compound 30 in CDCl $_3$ 



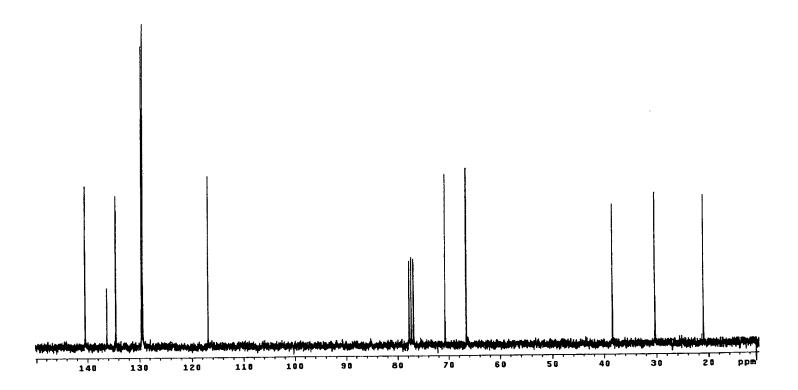
300MHz <sup>1</sup>H NMR of compound **31** in CDCl<sub>3</sub>



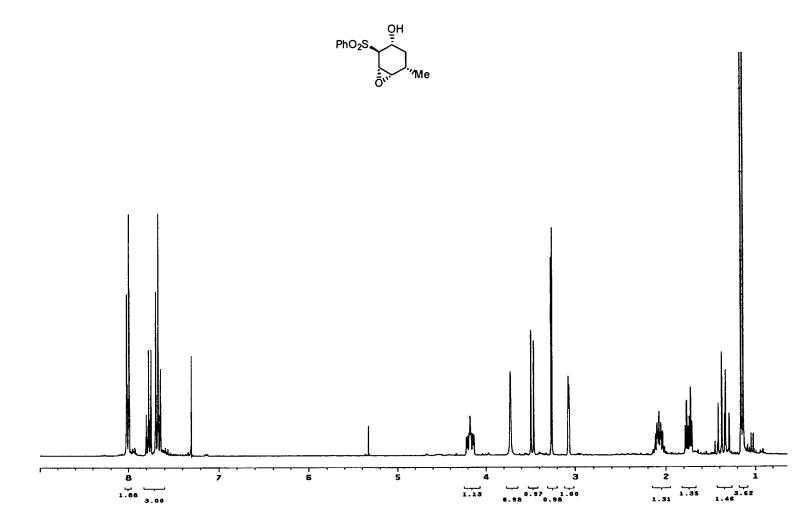
75MHz  $^{13}$ C NMR of compound 31 in CDCl $_3$ 



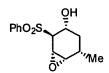
300MHz  $^1\mathrm{H}$  NMR of compound 32 in CDCl $_3$ 

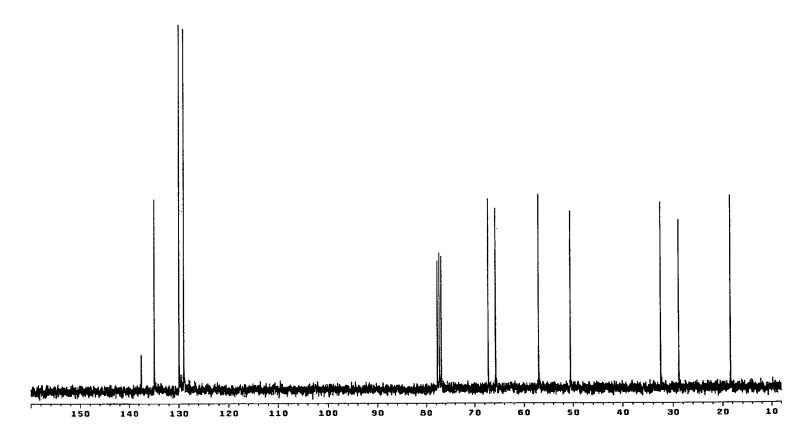


75MHz  $^{13}$ C NMR of compound 32 in CDCl $_3$ 

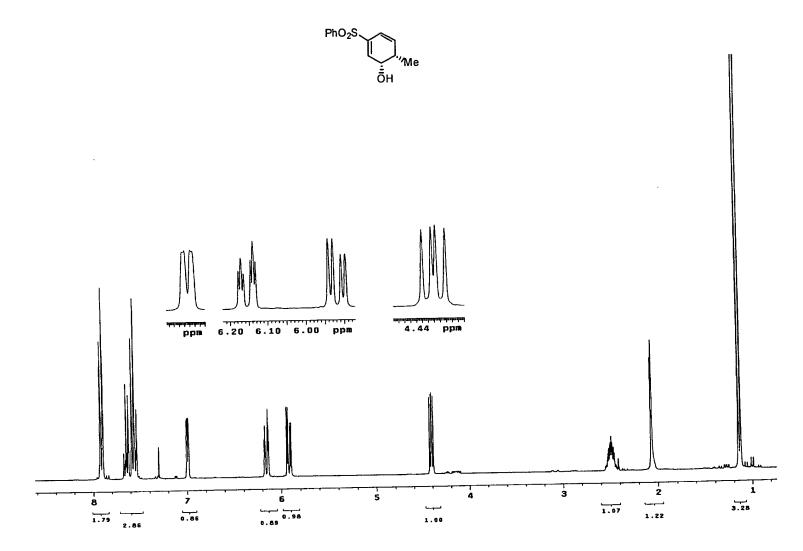


300MHz  $^1\mathrm{H}$  NMR of compound 33 in CDCl $_3$ 

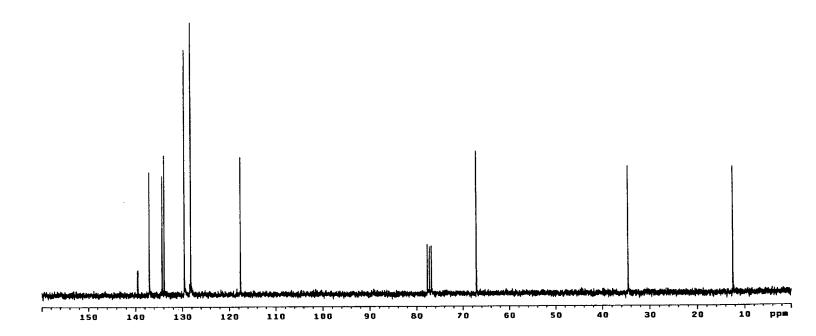




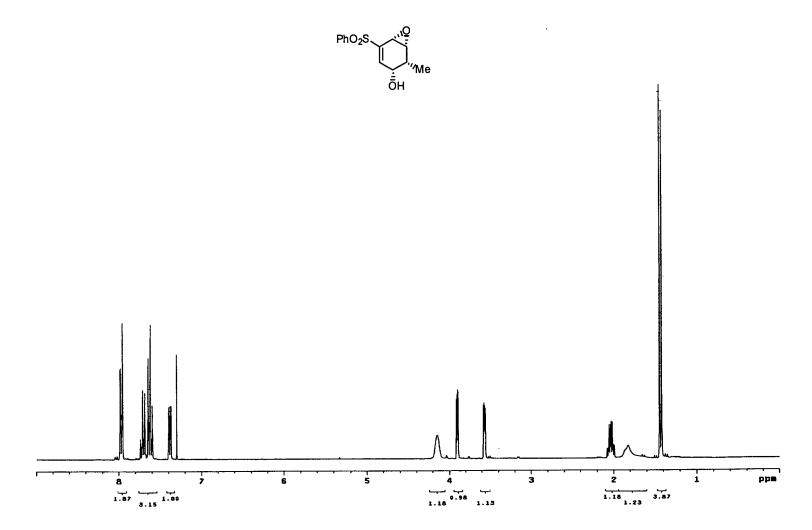
75MHz  $^{13}$ C NMR of compound 33 in CDCl $_3$ 



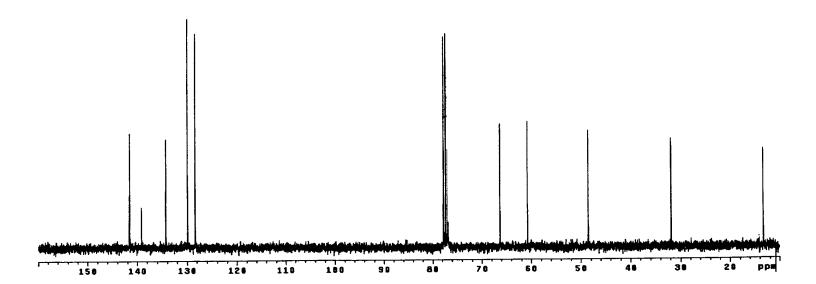
300MHz  $^1\mathrm{H}$  NMR of compound 35 in CDCl<sub>3</sub>



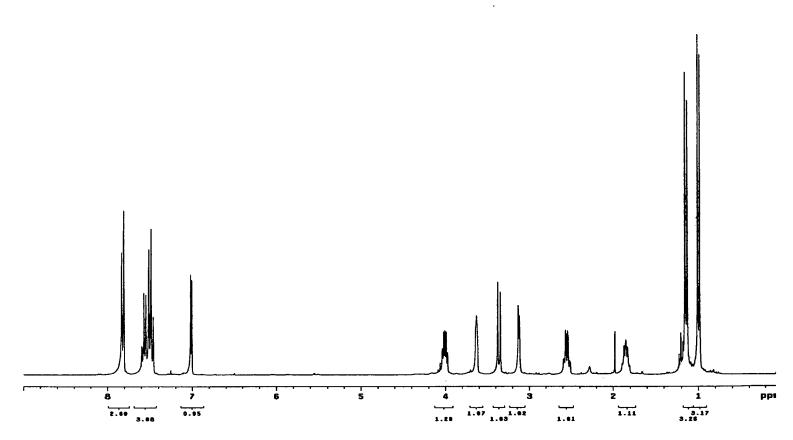
75MHz  $^{13}\mathrm{C}$  NMR of compound 35 in CDCl $_3$ 



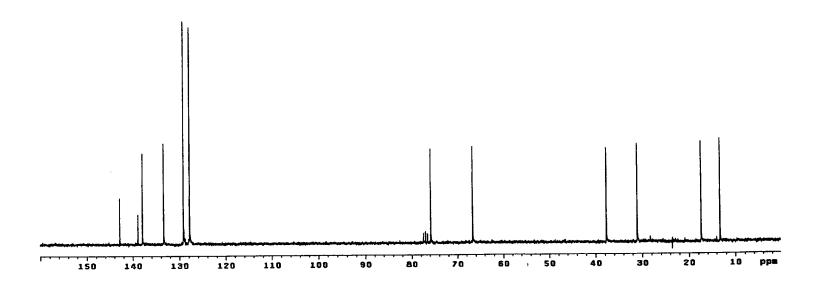
300MHz  $^1\mathrm{H}$  NMR of compound 36 in CDCl $_3$ 



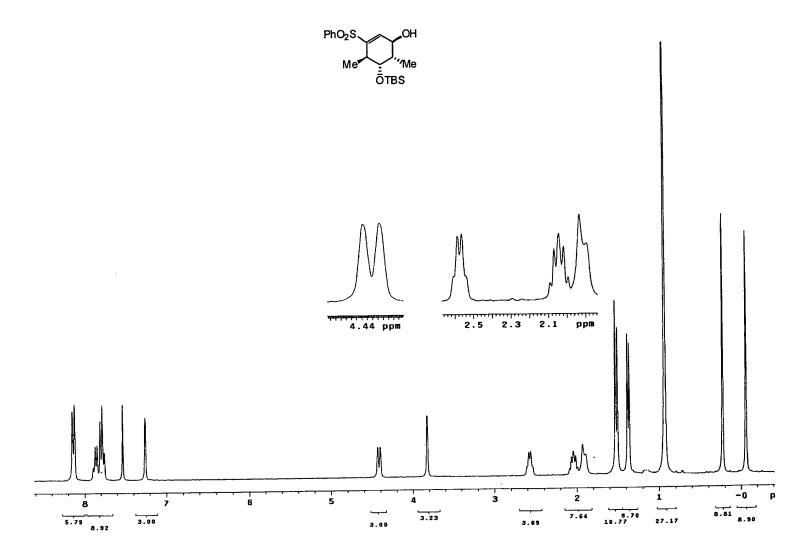
75MHz  $^{13}\mathrm{C}$  NMR of compound 36 in  $\mathrm{CDCl_3}$ 



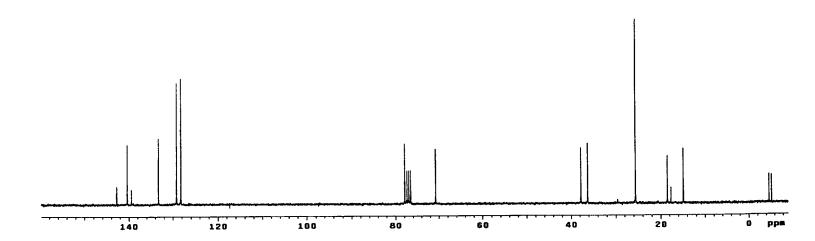
300MHz  $^1\mathrm{H}$  NMR of compound 37 in CDCl $_3$ 



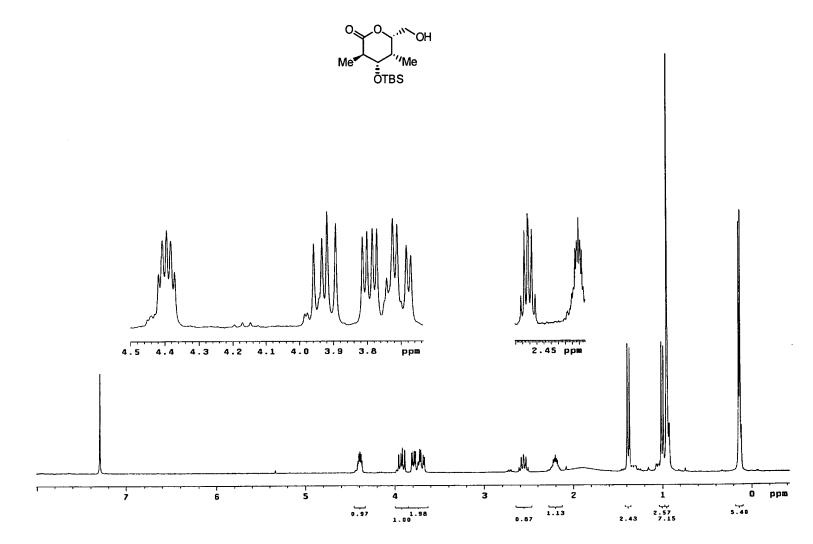
75MHz  $^{13}\mathrm{C}$  NMR of compound 37 in  $\mathrm{CDCl_3}$ 



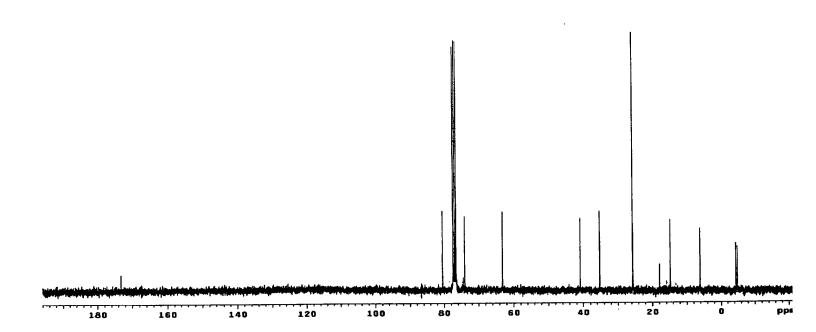
300MHz  $^1\mathrm{H}$  NMR of compound 38 in CDCl<sub>3</sub>



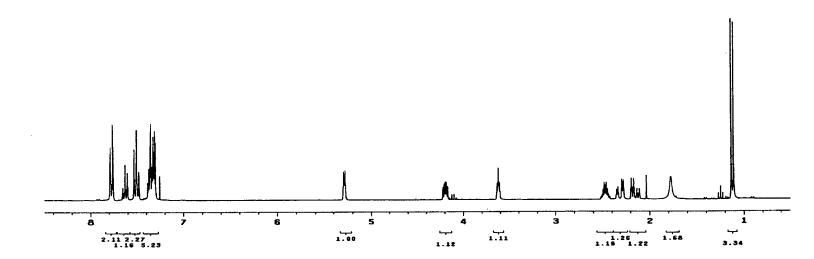
75MHz  $^{13}\mathrm{C}$  NMR of compound 38 in  $\mathrm{CDCl}_3$ 



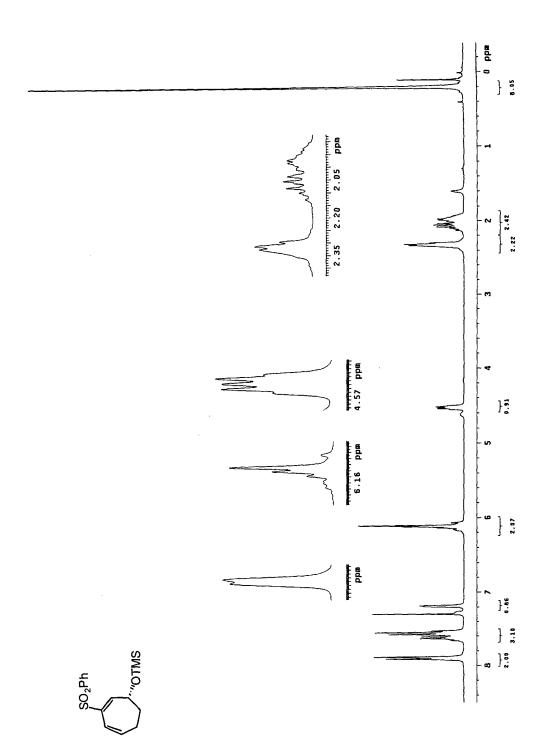
300MHz  $^1$ H NMR of compound 39 in CDCl<sub>3</sub>



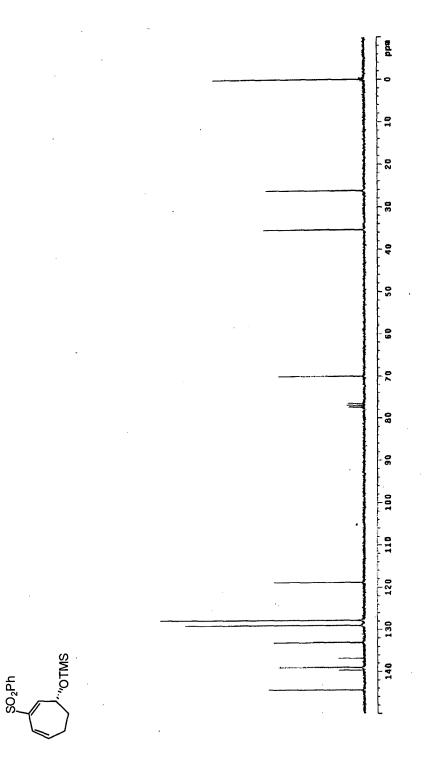
75MHz  $^{13}$ C NMR of compound 39 in CDCl $_3$ 



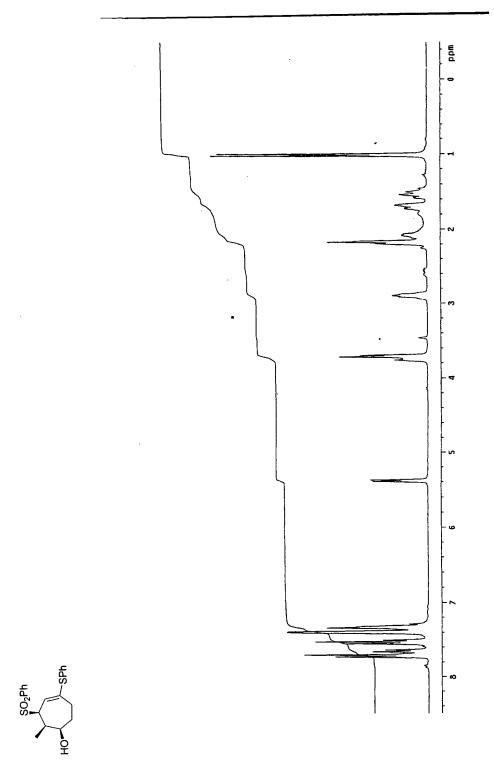
300MHz  $^1\text{H}$  NMR of compound  $43\beta$  in CDCl $_3$ 



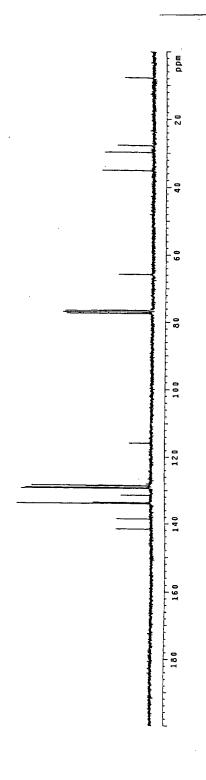
 $300 \mathrm{MHz}$  <sup>1</sup>H NMR of compound 13 in CDCl<sub>3</sub>



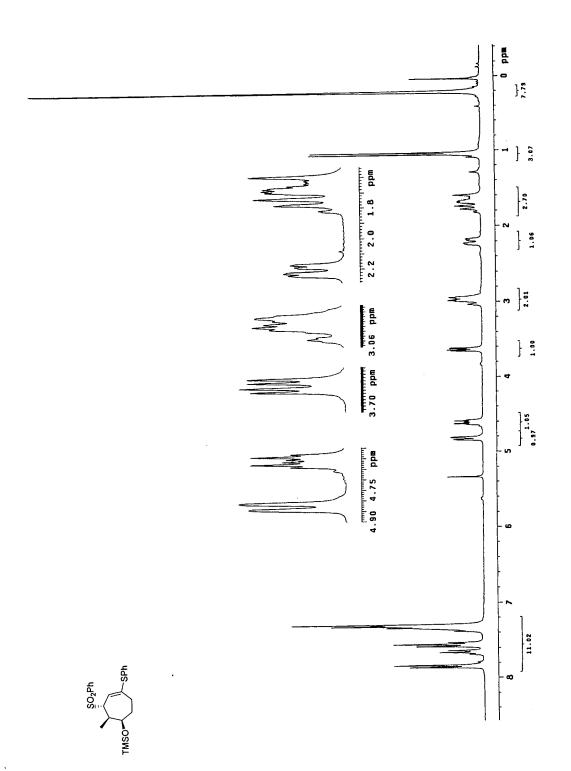
75MHz <sup>13</sup>C NMR of compound 13 in CDCl<sub>3</sub>



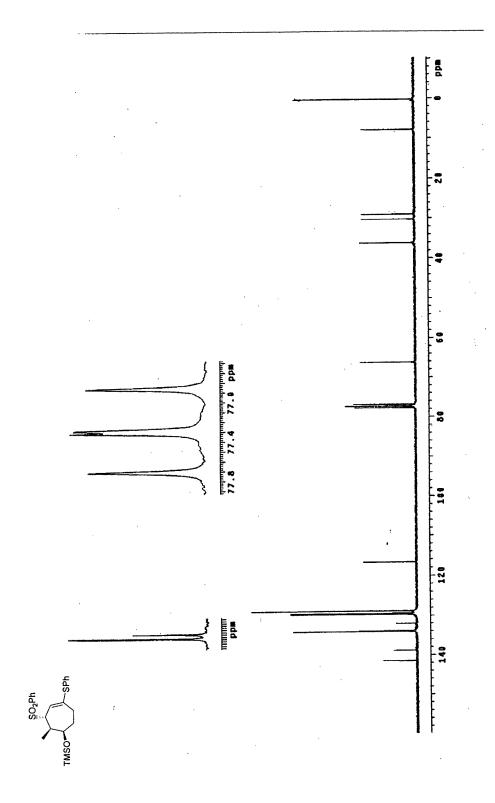
300MHz  $^1\mathrm{H}$  NMR of compound 21 in CDCl  $_3$ 



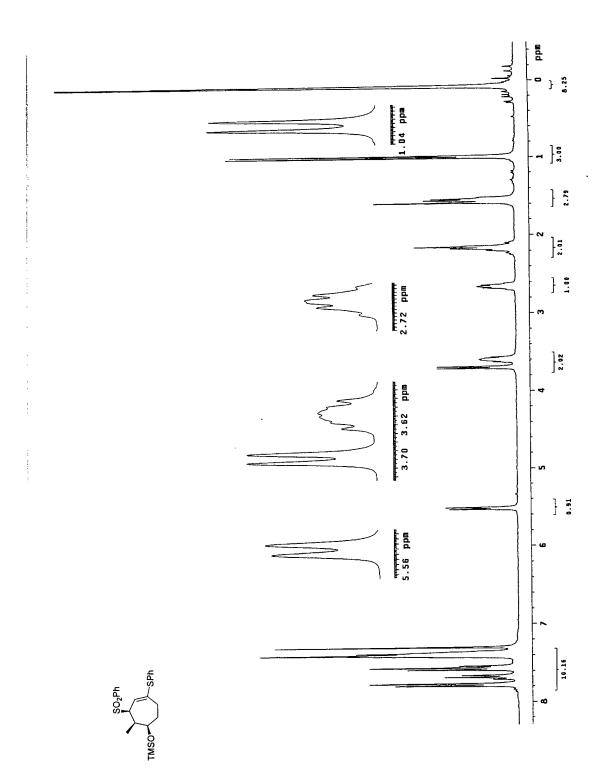
75MHz  $^{13}\mathrm{C}$  NMR of compound 21 in CDCl  $_3$ 



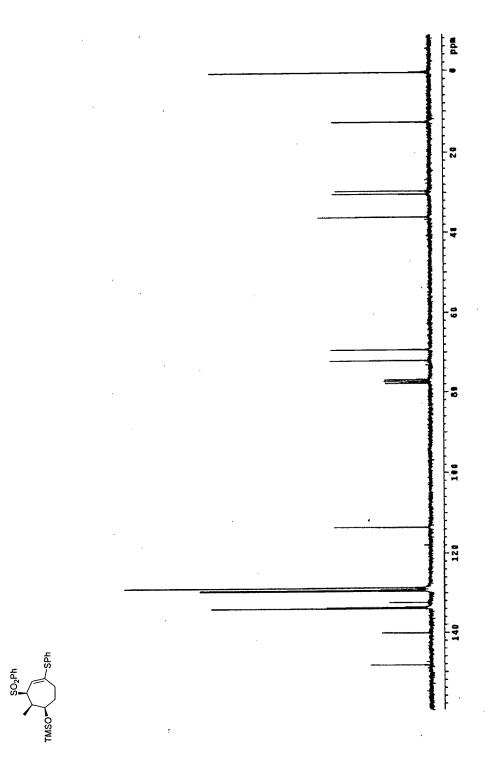
300MHz  $^1\mathrm{H}$  NMR of compound 23  $\alpha$  in CDCl  $_3$ 



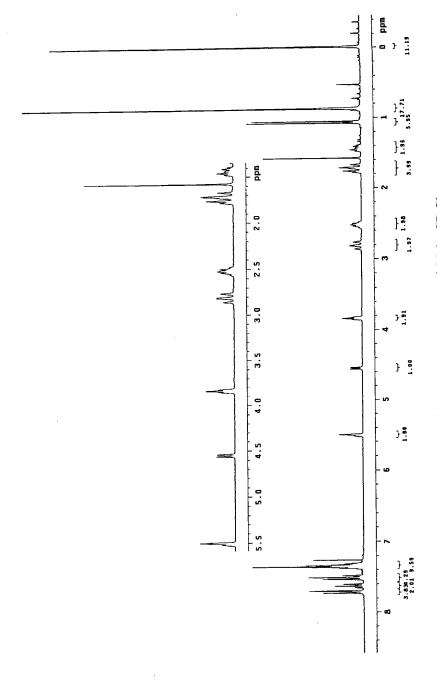
75MHz  $^{13}\text{C}$  NMR of compound 23  $\alpha$  in CDCl  $_3$ 



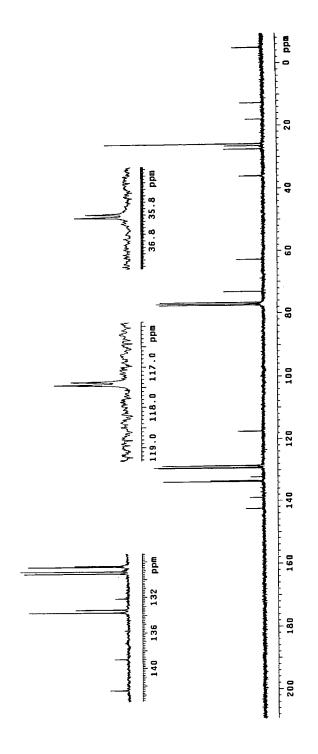
300MHz  $^1 H$  NMR of compound 23  $\beta$  in CDCl  $_3$ 



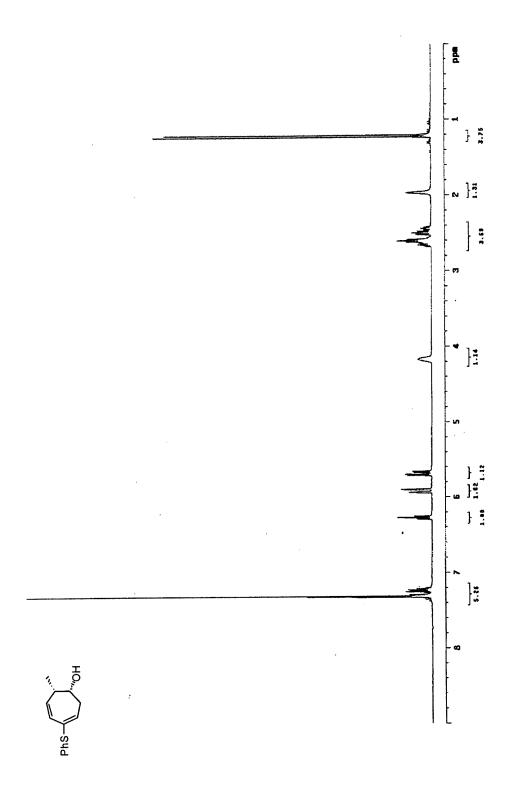
75MHz  $^{13}\text{C}$  NMR of compound 23  $\beta$  in CDCl  $_3$ 



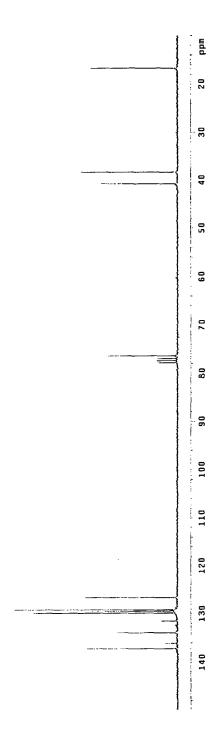
 $300 \mathrm{MHz}$   $^{1}\mathrm{H}$  NMR of compound 22 in CDCl  $_{3}$ 



75MHz  $^{13}\mathrm{C}$  NMR of compound 22 in CDCl  $_3$ 

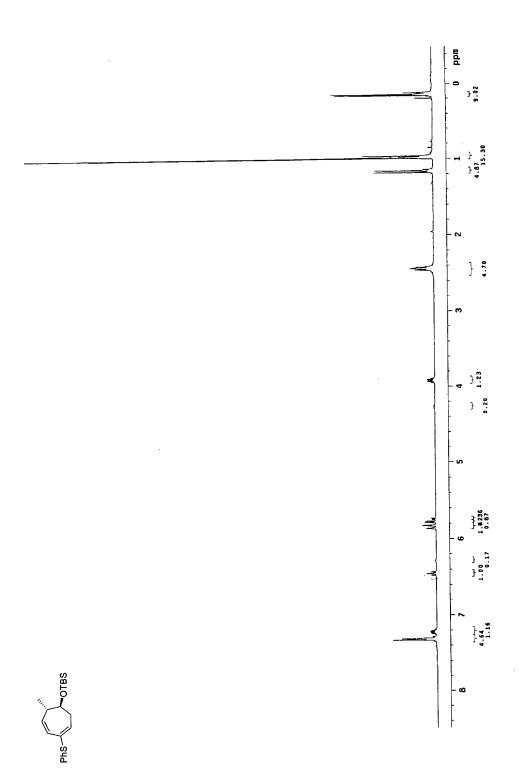


300 MHz  $^1\mathrm{H}$  NMR of compound 29 in CDCl  $_3$ 

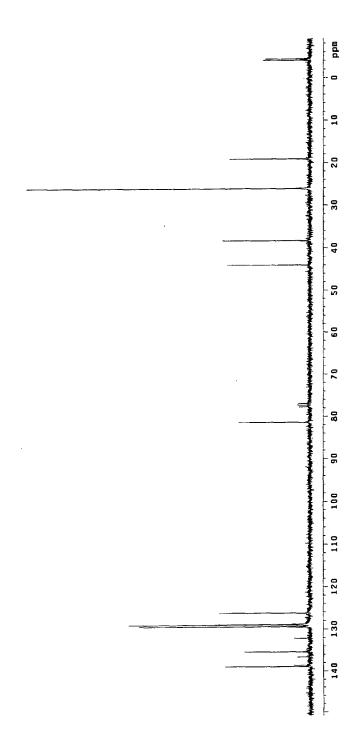


75MHz  $^{13}\mathrm{C}$  NMR of compound 29 in CDCl  $_3$ 

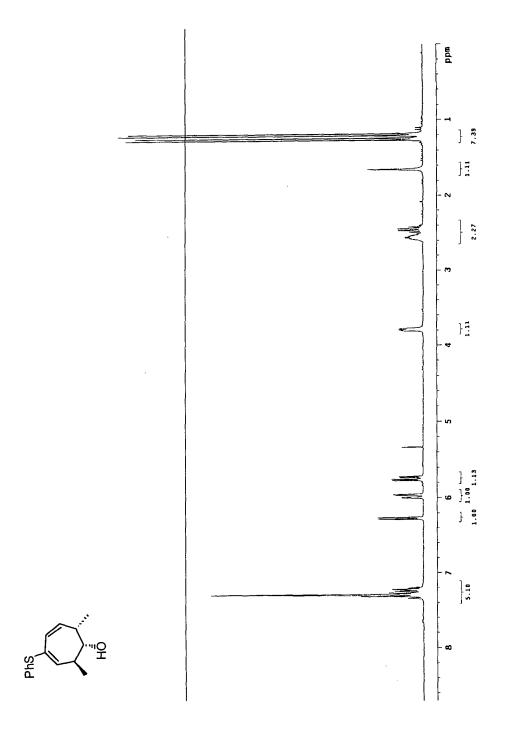




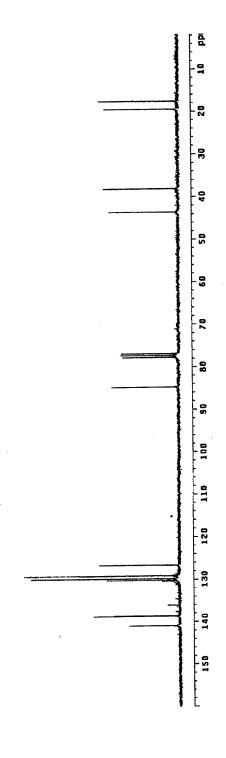
 $300 \mathrm{MHz}$  <sup>1</sup>H NMR of compound 27 in CDCl <sub>3</sub>



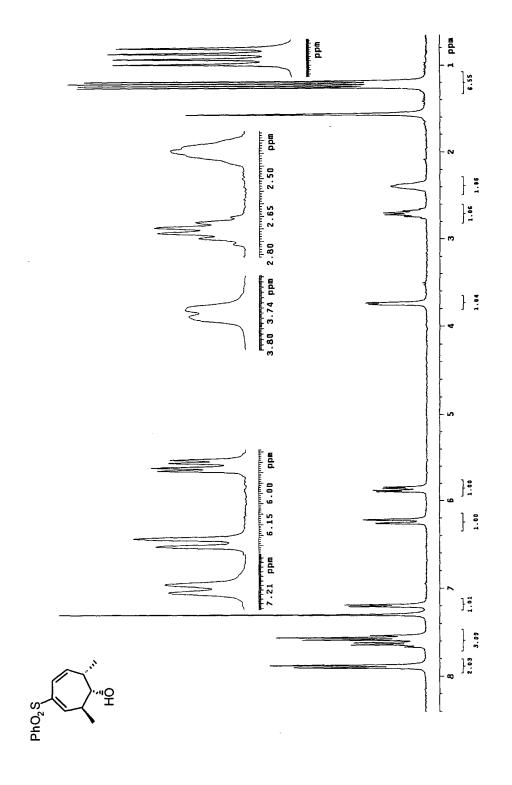
75MHz  $^{13}\mathrm{C}$  NMR of compound 27 in CDCl  $_3$ 



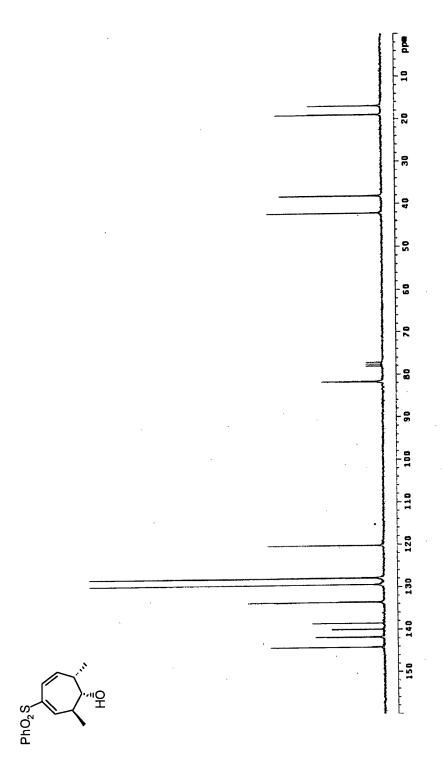
 $300 \mathrm{MHz}\ ^{1}\mathrm{H}\ \mathrm{NMR}$  of compound  $31\ \mathrm{in}\ \mathrm{CDCl_{3}}$ 



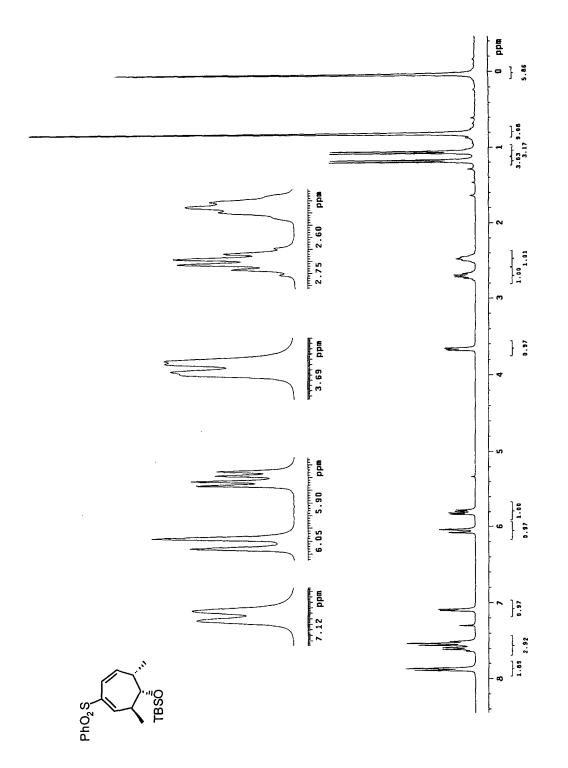
 $75 \mathrm{MHz}$   $^{13}\mathrm{C}$  NMR of compound 31 in CDCl<sub>3</sub>



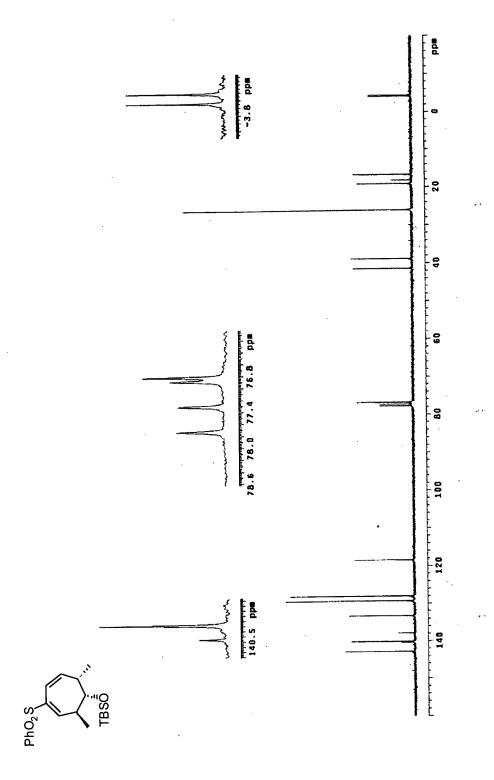
 $300 \mathrm{MHz}$   $^{1}\mathrm{H}$  NMR of compound 32 in CDCl $_{3}$ 



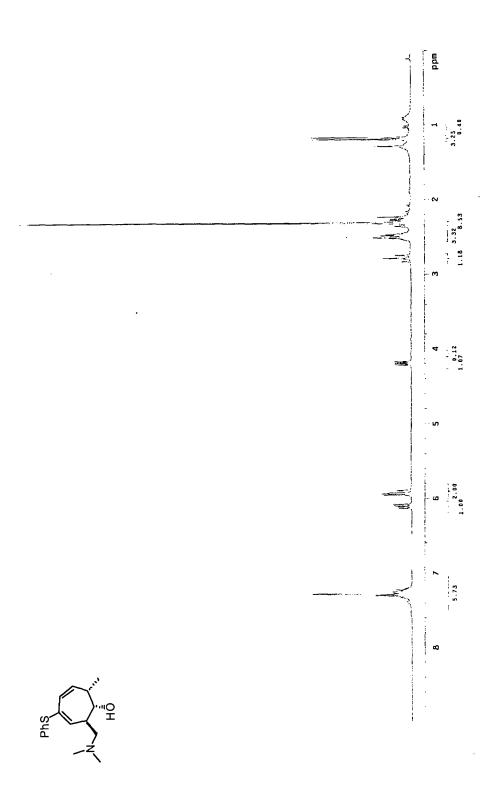
75MHz <sup>13</sup>C NMR of compound 32 in CDCl<sub>3</sub>



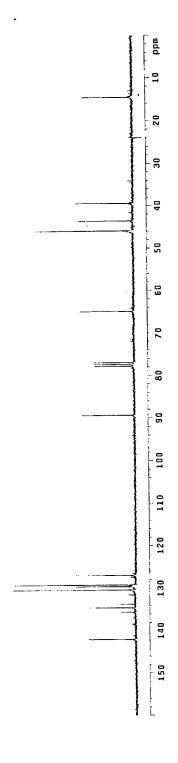
 $300 \mathrm{MHz}$  <sup>1</sup>H NMR of compound 33 in CDCl<sub>3</sub>



75MHz  $^{13}$ C NMR of compound 33 in CDCl $_3$ 

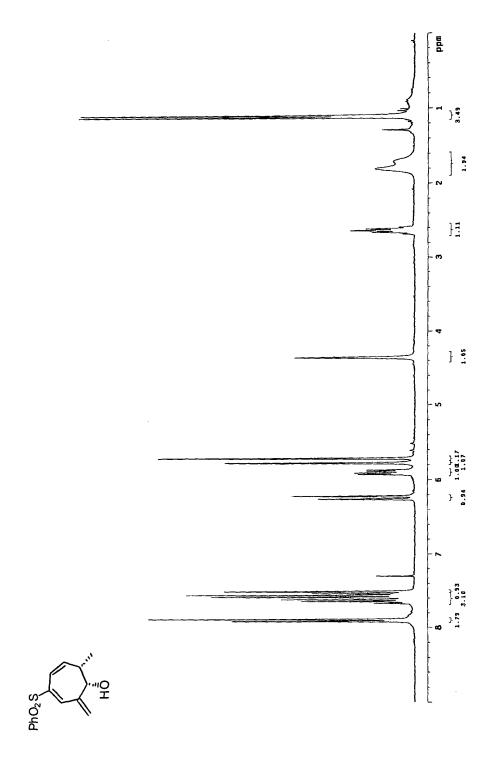


300MHz <sup>1</sup>H NMR of compound 34 in CDCl<sub>3</sub>

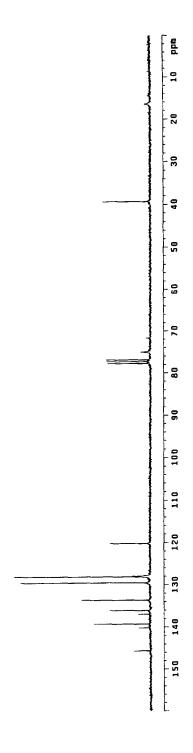


75MHz  $^{13}\mathrm{C}$  NMR of compound 34 in CDCl<sub>3</sub>

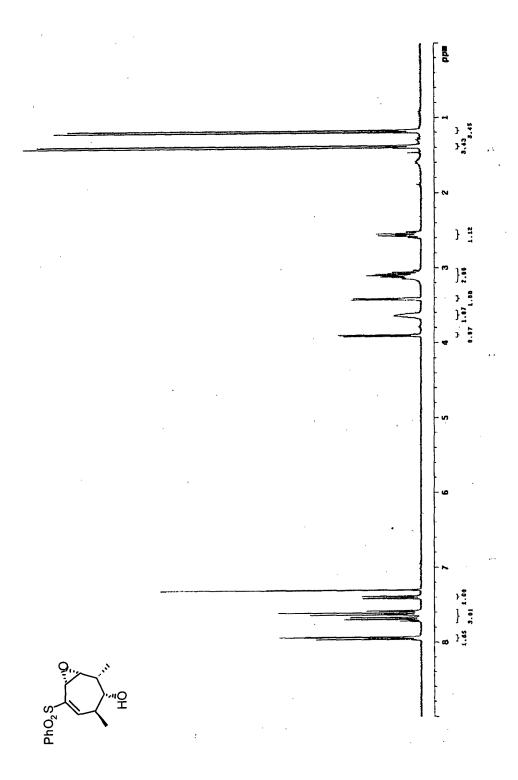




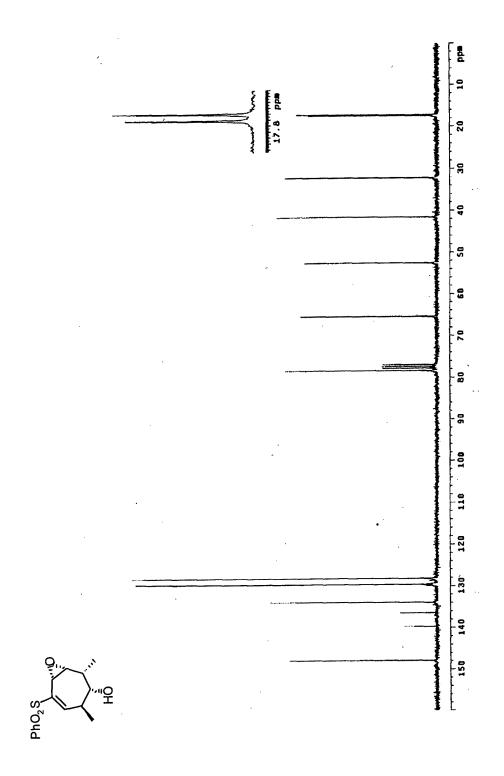
 $300 \mathrm{MHz}$  <sup>1</sup>H NMR of compound 35 in CDCl<sub>3</sub>



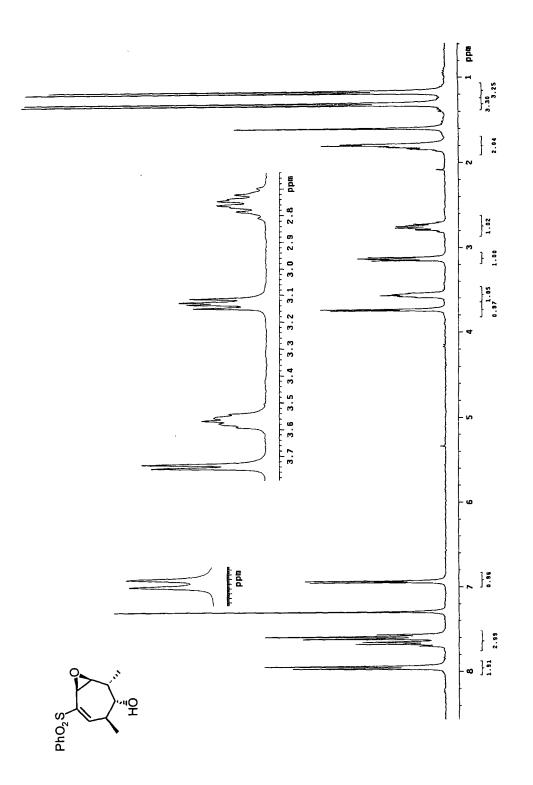
75MHz  $^{13}$ C NMR of compound 35 in CDCl $_3$ 



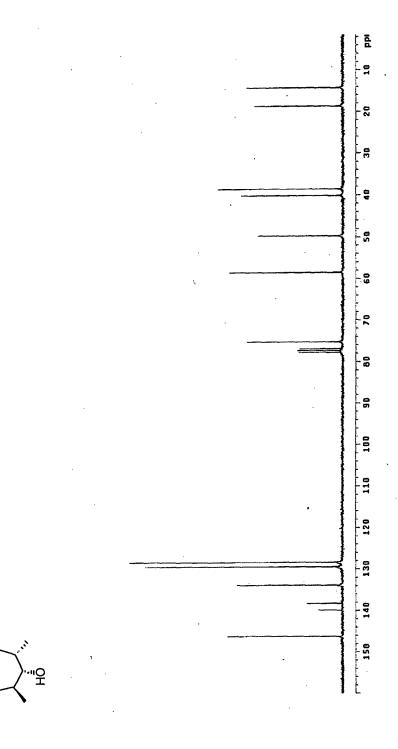
300MHz  $^1\text{H}$  NMR of compound  $\alpha 36$  in CDCl $_3$ 



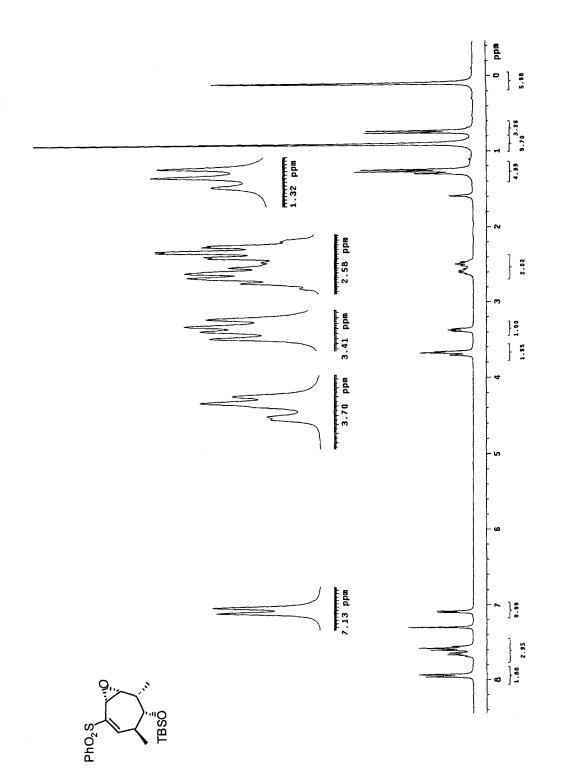
75MHz  $^{\rm 13}C$  NMR of compound  $\alpha 36$  in CDCl $_{\rm 3}$ 



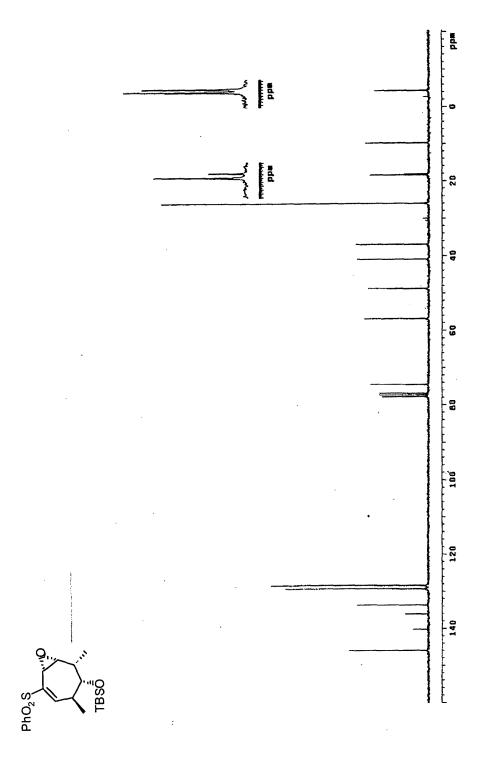
 $300 MHz\ ^1 H\ NMR$  of compound  $\beta 36\ in\ CDCl_3$ 



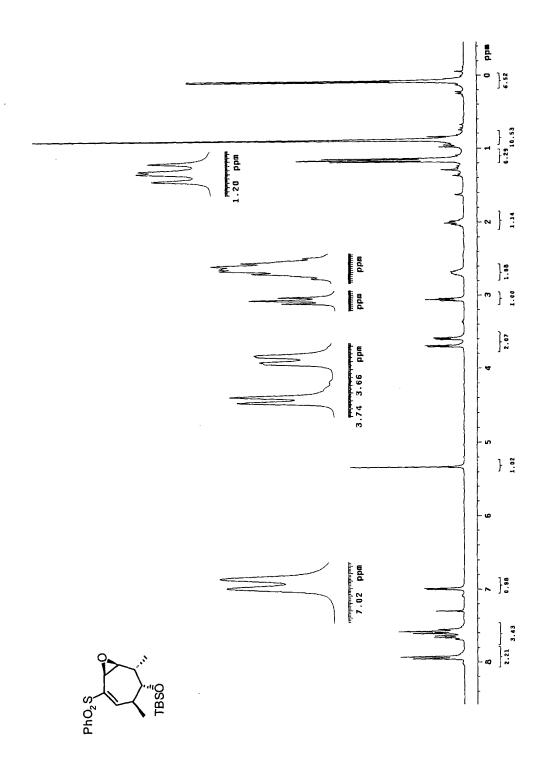
75MHz  $^{\rm 13}C$  NMR of compound  $\beta 36$  in CDCl $_{\rm 3}$ 



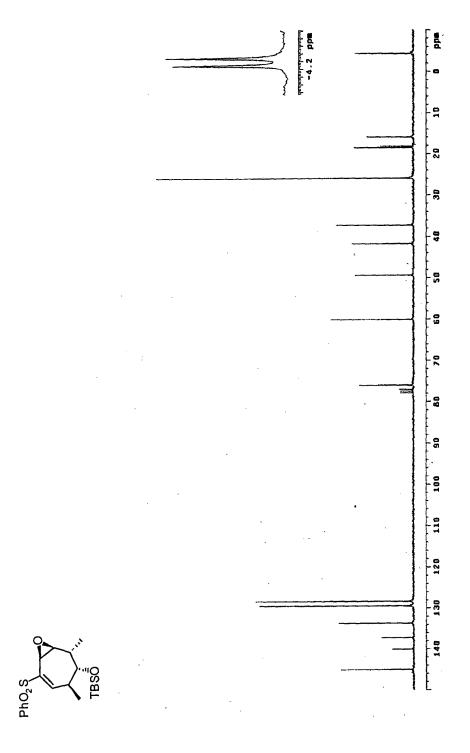
300MHz  $^{\rm l}H$  NMR of compound  $\alpha37$  in CDCl $_{\rm 3}$ 



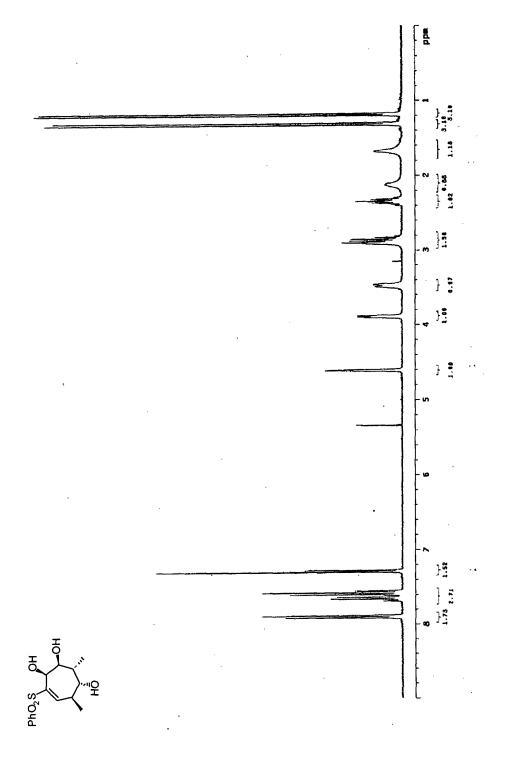
75MHz  $^{13}\text{C}$  NMR of compound  $\alpha37$  in CDCl $_3$ 



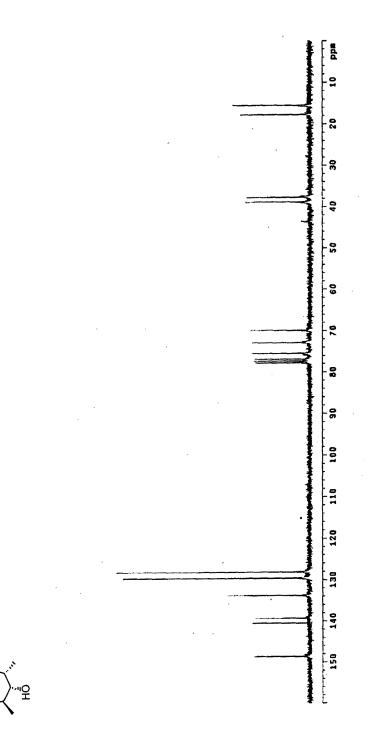
 $300 MHz\ ^1 H$  NMR of compound  $\beta 37$  in CDCl $_3$ 



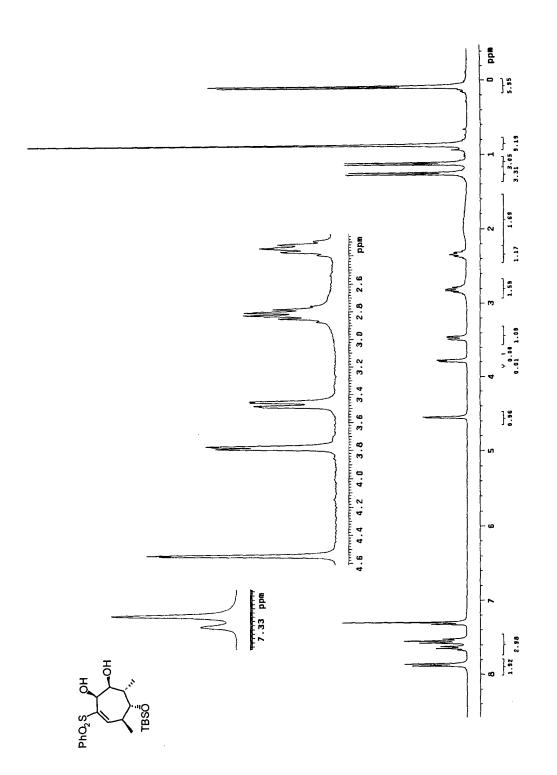
75MHz  $^{13}\text{C}$  NMR of compound  $\beta37$  in CDCl $_3$ 



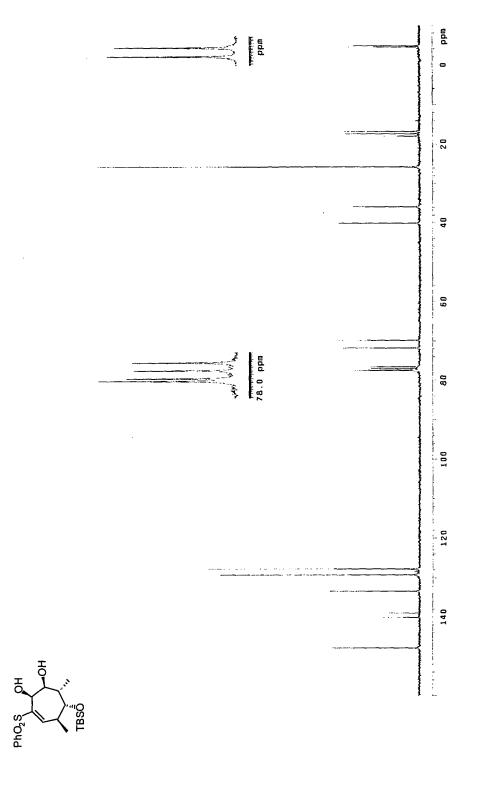
 $300 \mathrm{MHz}$  <sup>1</sup>H NMR of compound 38 in CDCl<sub>3</sub>



75MHz <sup>13</sup>C NMR of compound 38 in CDCl<sub>3</sub>

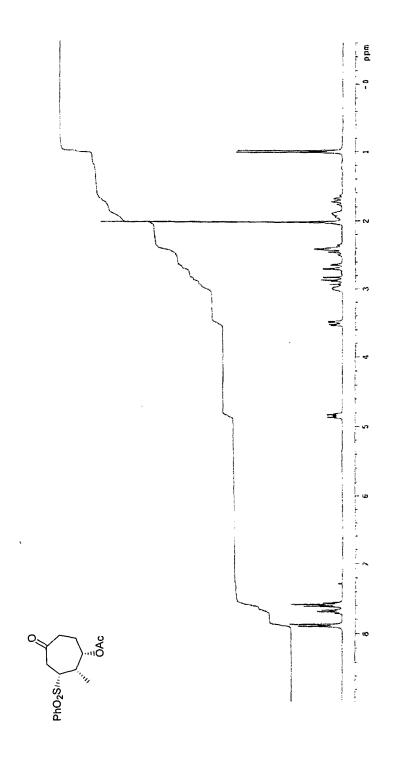


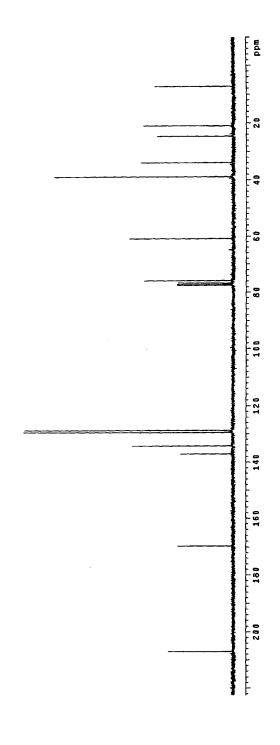
 $300\mbox{MHz}\ ^{1}\mbox{H}\ \mbox{NMR}$  of compound 39 in  $\mbox{CDCI}_{3}$ 



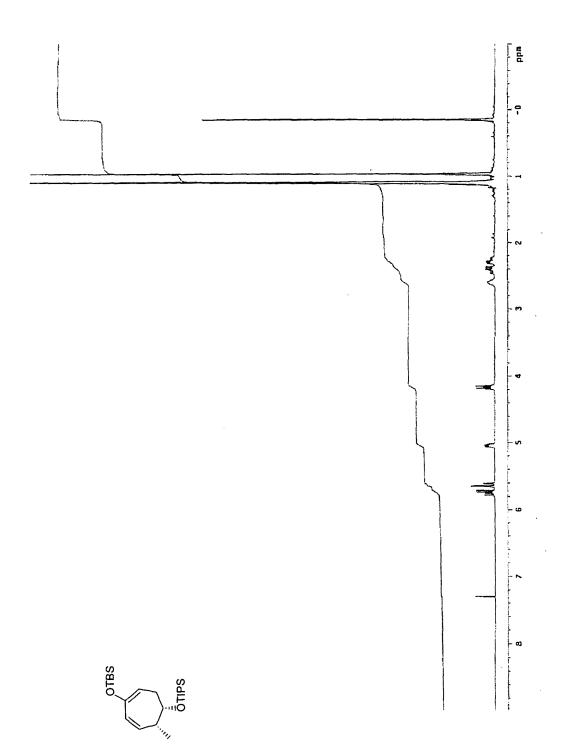
75MHz  $^{13}$ C NMR of compound 39 in CDCl $_3$ 



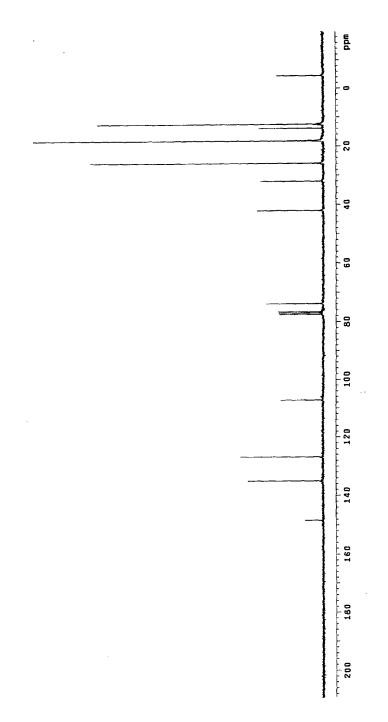




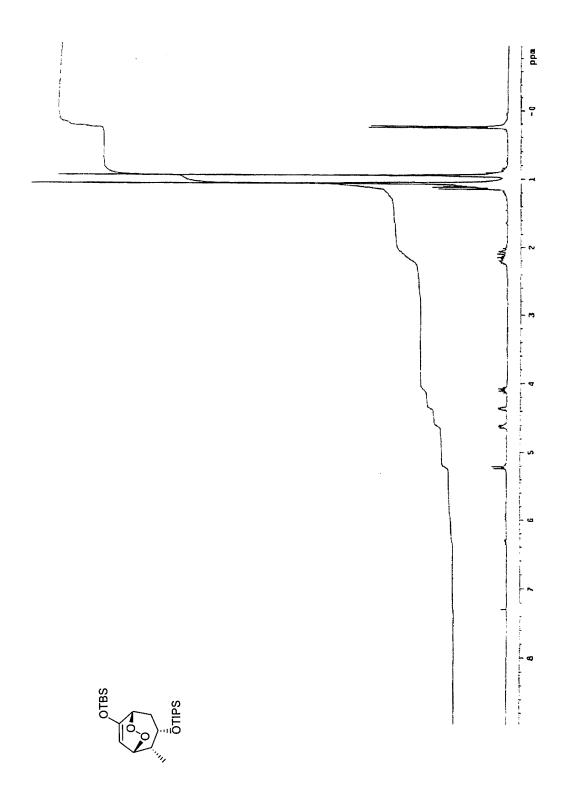
75MHz  $^{13}\mathrm{C}$  NMR of compound 41 in CDCl $_3$ 



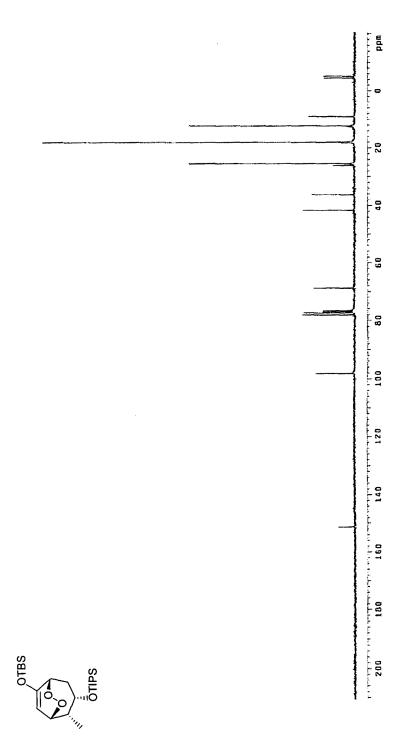
 $300\mbox{MHz}$   $^{1}\mbox{H}$  NMR of compound 42 in CDCl $_{3}$ 



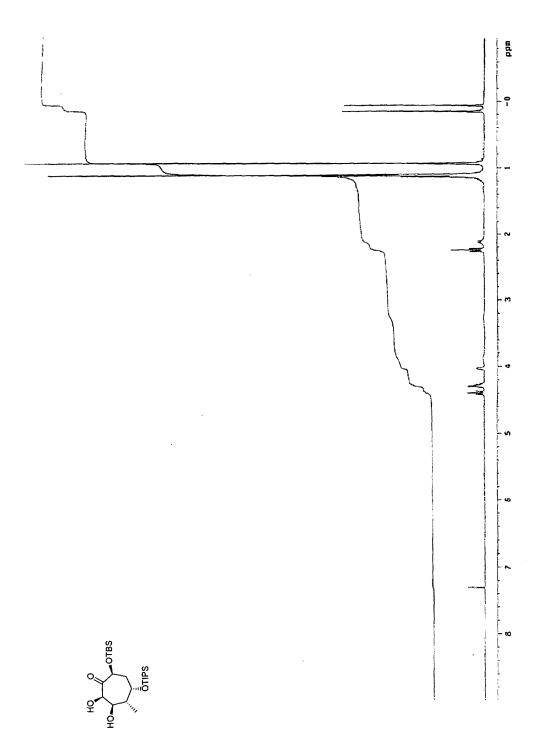
75MHz  $^{13}$ C NMR of compound 42 in CDCl $_3$ 



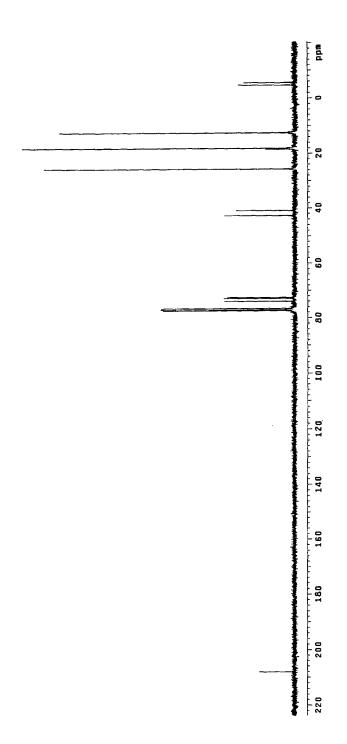
 $300 \mathrm{MHz}$  <sup>1</sup>H NMR of compound 43 in CDCl<sub>3</sub>



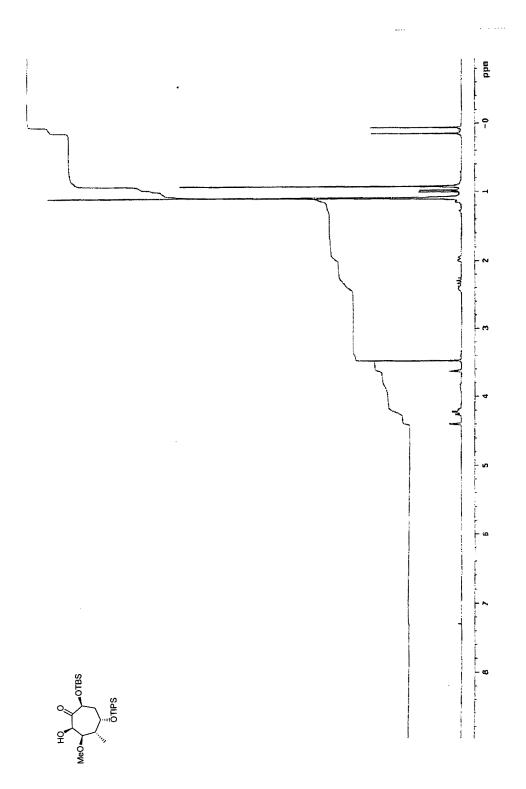
75MHz  $^{13}$ C NMR of compound 43 in CDCl $_3$ 



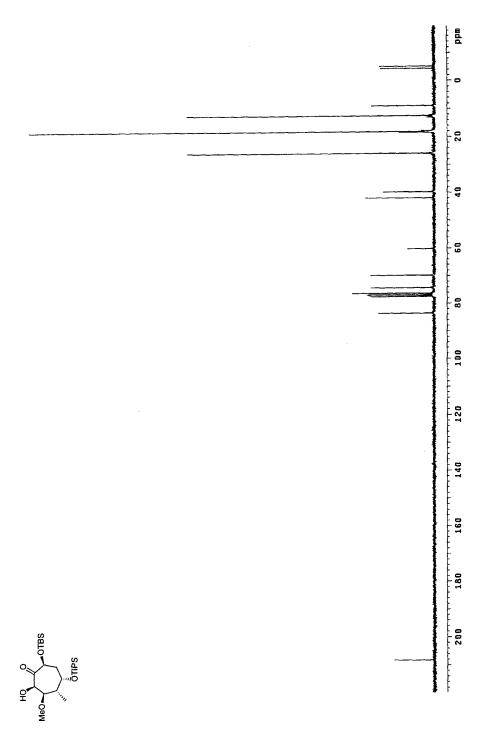
 $300\mbox{MHz}\ ^{1}\mbox{H}\ \mbox{NMR}$  of compound 46 in  $\mbox{CDCl}_{3}$ 



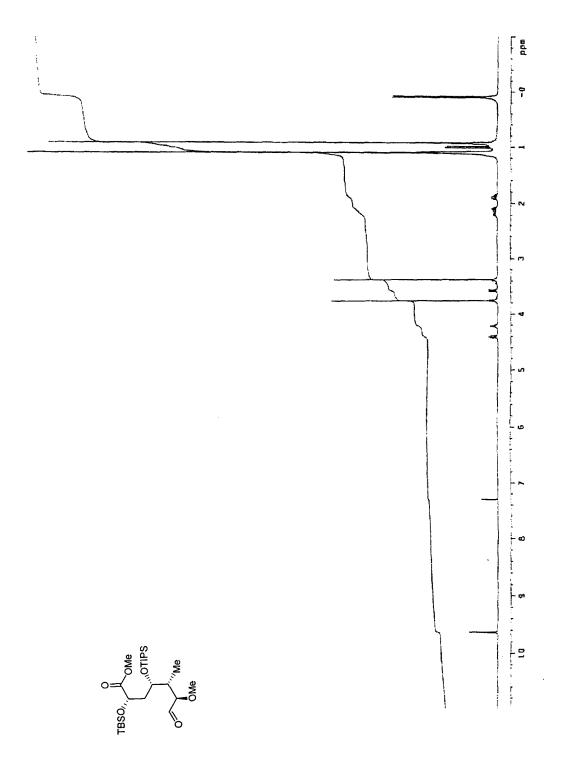
75MHz  $^{13}$ C NMR of compound 46 in CDCl $_3$ 



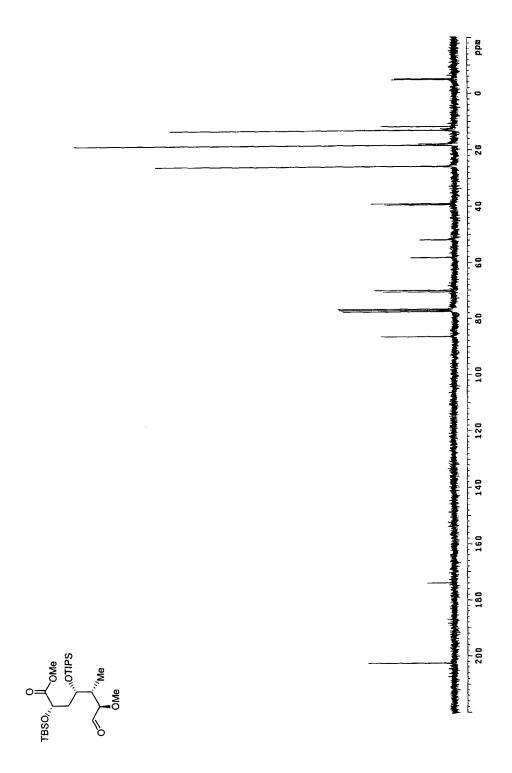
 $300 \mathrm{MHz}$  <sup>1</sup>H NMR of compound 47 in CDCl<sub>3</sub>



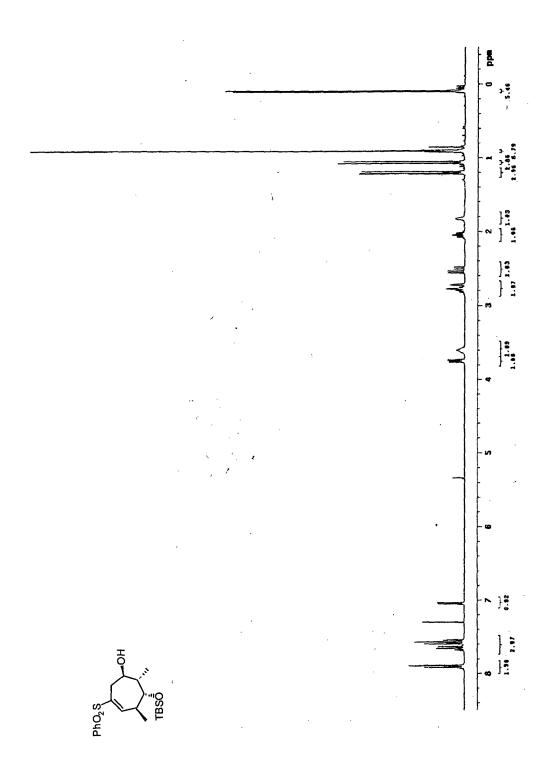
75MHz <sup>13</sup>C NMR of compound 47 in CDCl<sub>3</sub>



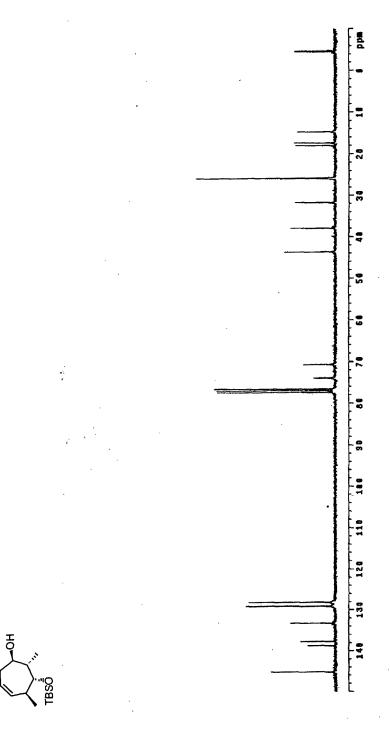
300MHz <sup>1</sup>H NMR of compound 48 in CDCl<sub>3</sub>



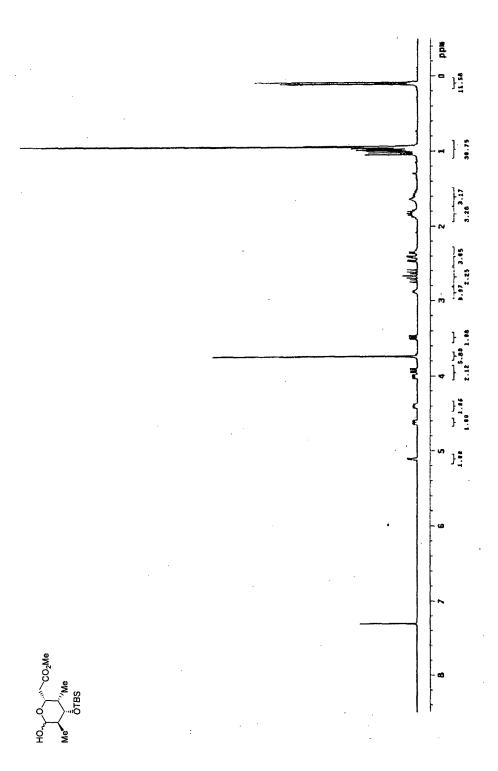
75MHz <sup>13</sup>C NMR of compound 48 in CDCl<sub>3</sub>



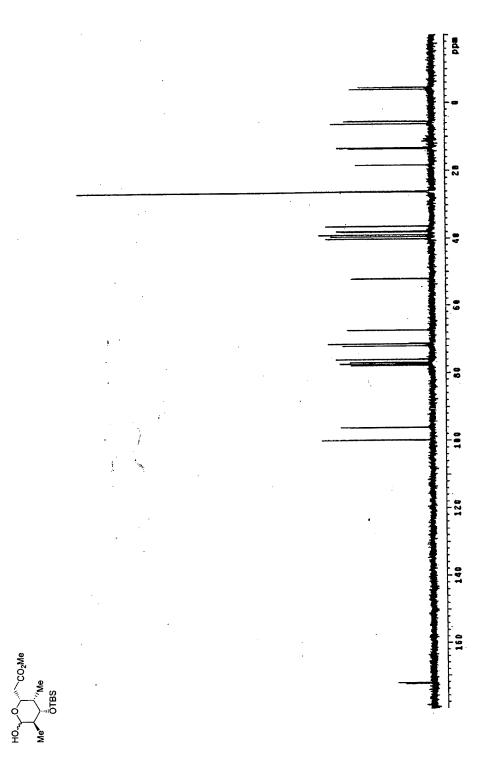
 $300 \mathrm{MHz}\ ^{1}\mathrm{H}\ \mathrm{NMR}$  of compound  $56\ \mathrm{in}\ \mathrm{CDCl_{3}}$ 



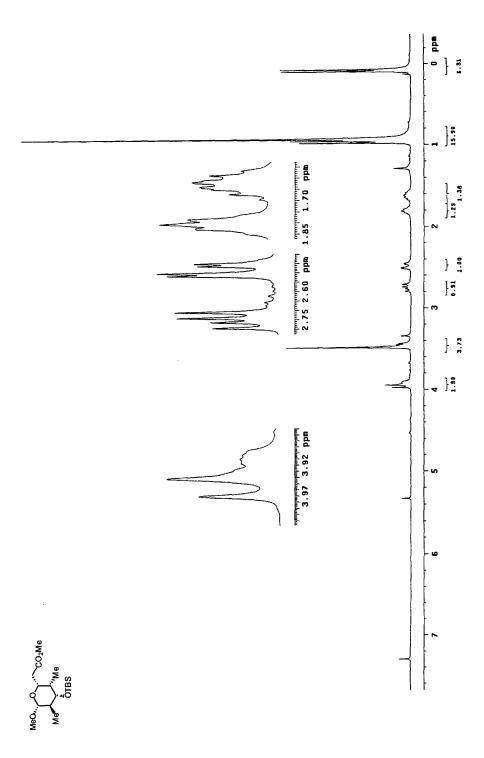
75MHz  $^{13}$ C NMR of compound 56 in CDCl<sub>3</sub>



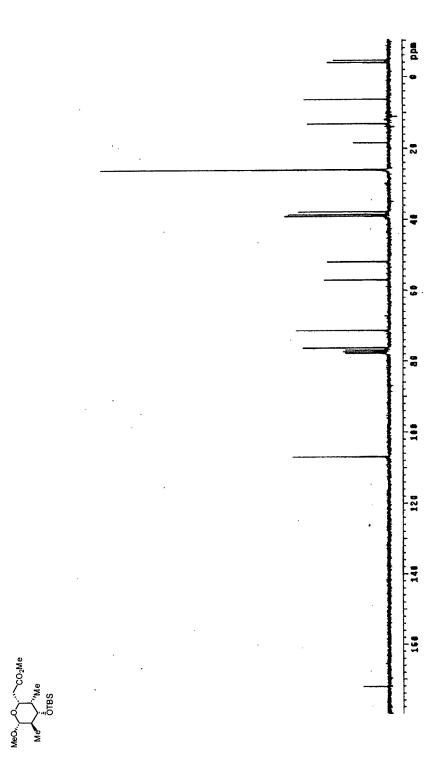
 $300 \mathrm{MHz}\ ^{1}\mathrm{H}\ \mathrm{NMR}$  of compound 57 in  $\mathrm{CDCl_{3}}$ 



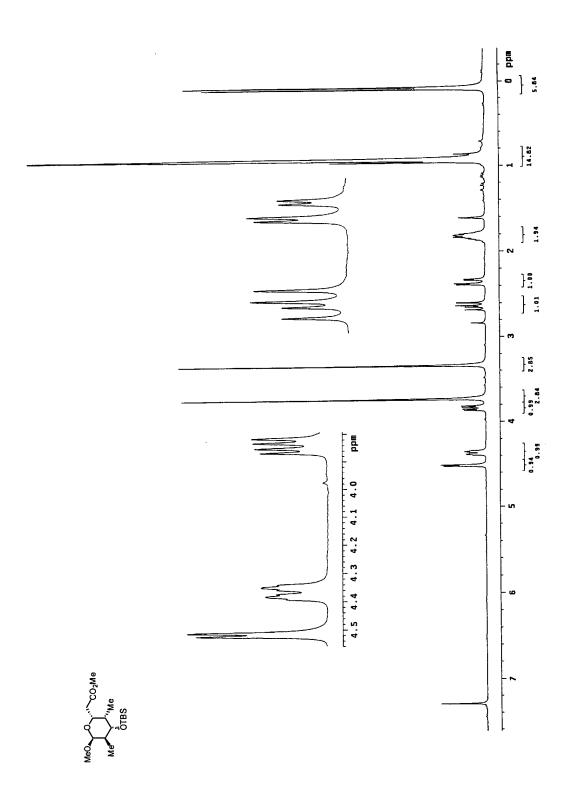
75MHz  $^{13}$ C NMR of compound 57 in CDCl $_3$ 



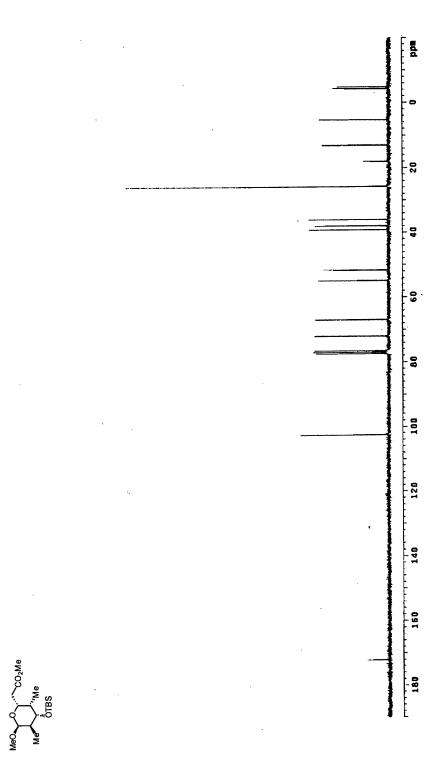
 $300 MHz\ ^1 H\ NMR$  of compound  $58\alpha$  in  $CDCl_3$ 



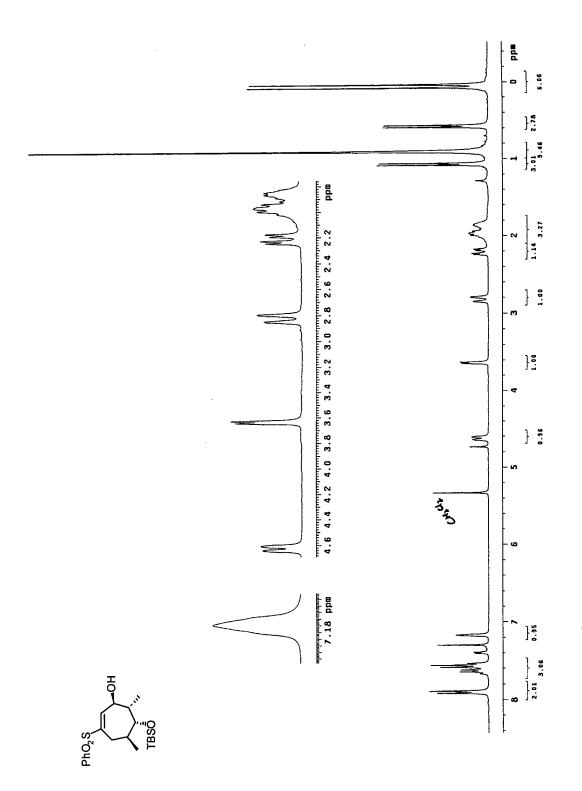
75MHz  $^{13}\text{C}$  NMR of compound  $58\alpha$  in CDCl $_3$ 



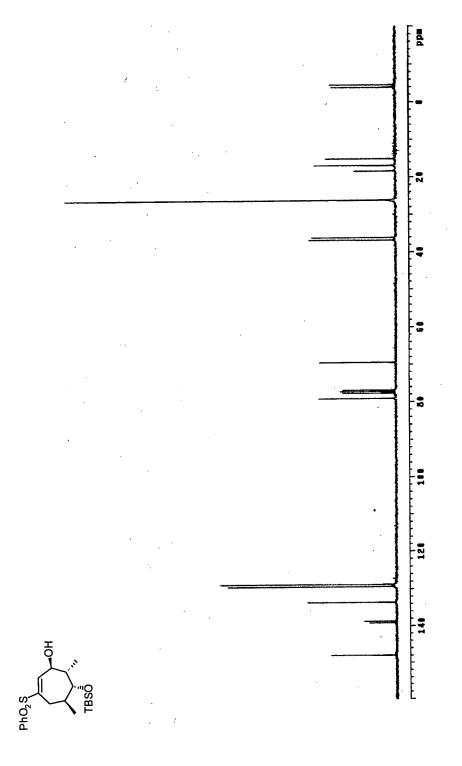
300MHz  $^{1}$ H NMR of compound  $58\beta$  in CDCl<sub>3</sub>



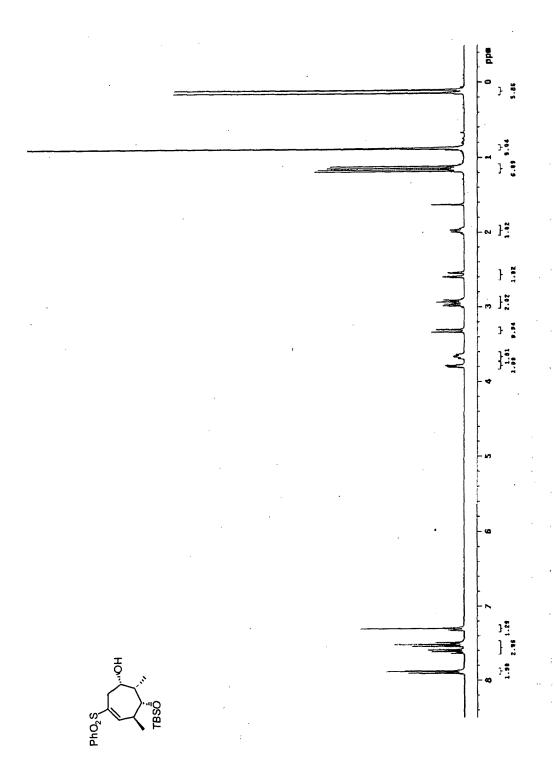
75MHz  $^{13}\text{C}$  NMR of compound 58 $\beta$  in CDCl $_3$ 



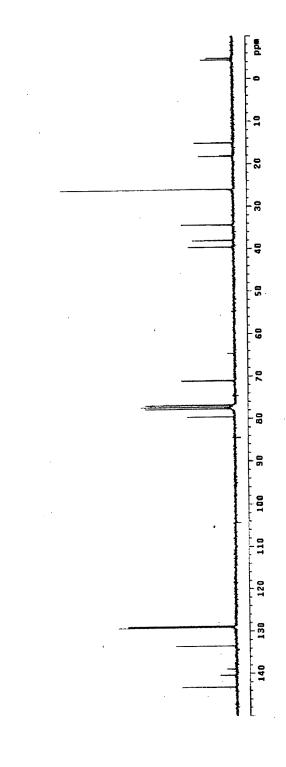
300MHz  $^{\rm 1}{\rm H}$  NMR of compound 59 in CDCl $_{\rm 3}$ 



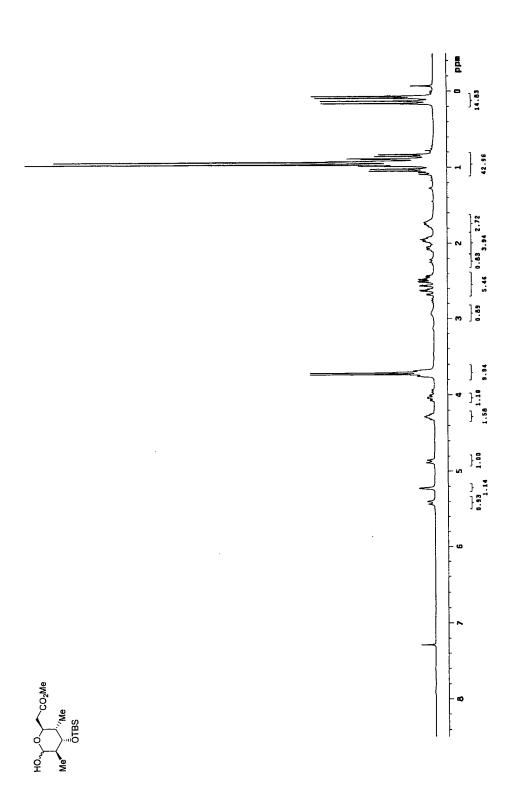
75MHz  $^{13}$ C NMR of compound 59 in CDCl $_3$ 



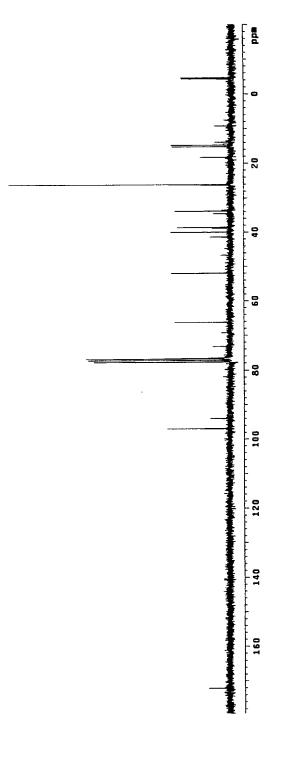
 $300 \mathrm{MHz}$   $^{1}\mathrm{H}$  NMR of compound 60 in CDCl $_{3}$ 



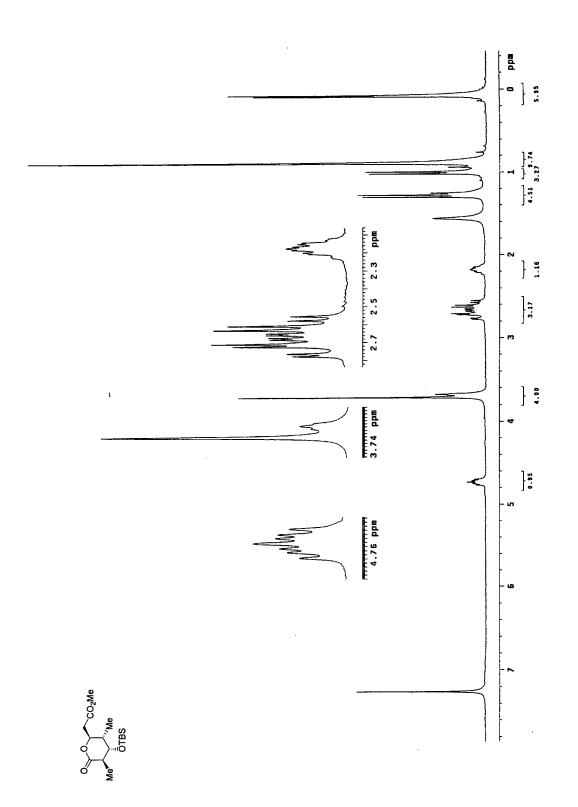
75MHz  $^{13}\mathrm{C}$  NMR of compound 60 in CDCl $_3$ 



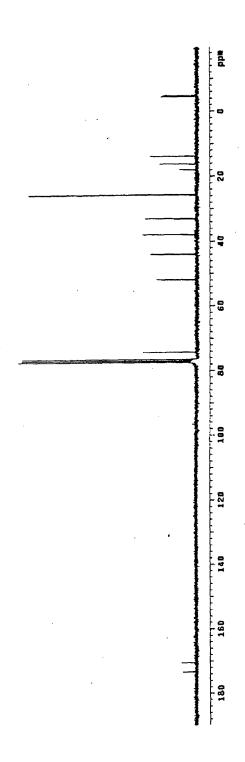
 $300 \mathrm{MHz}$  <sup>1</sup>H NMR of compound 61 in CDCl<sub>3</sub>



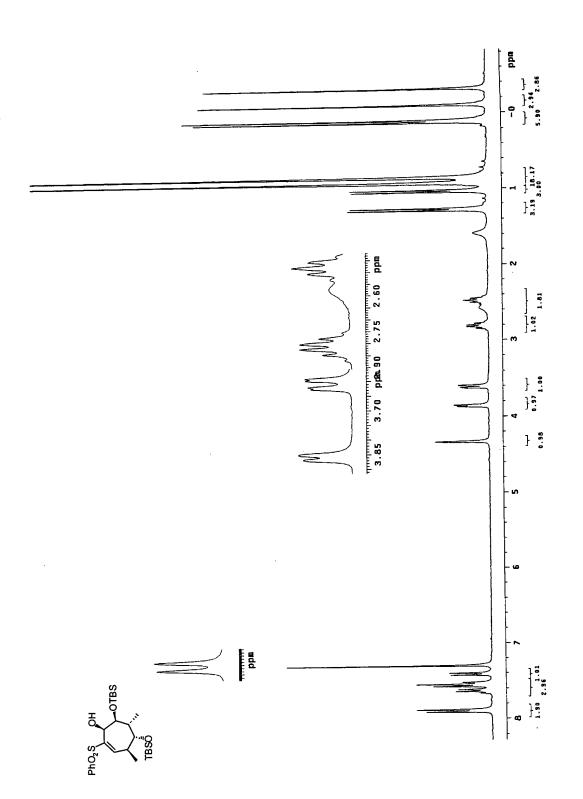
 $75 \mathrm{MHz}$   $^{13}\mathrm{C}$  NMR of compound 61 in CDCl $_3$ 



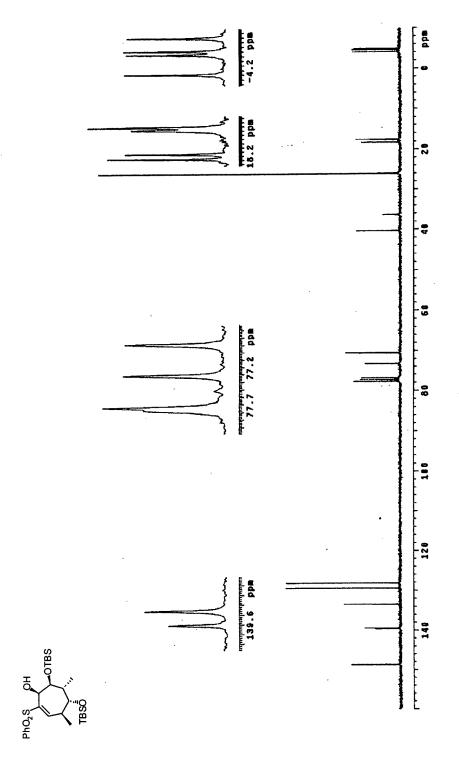
 $300 \mathrm{MHz}\ ^{1}\mathrm{H}\ \mathrm{NMR}$  of compound 62 in CDCl $_{3}$ 



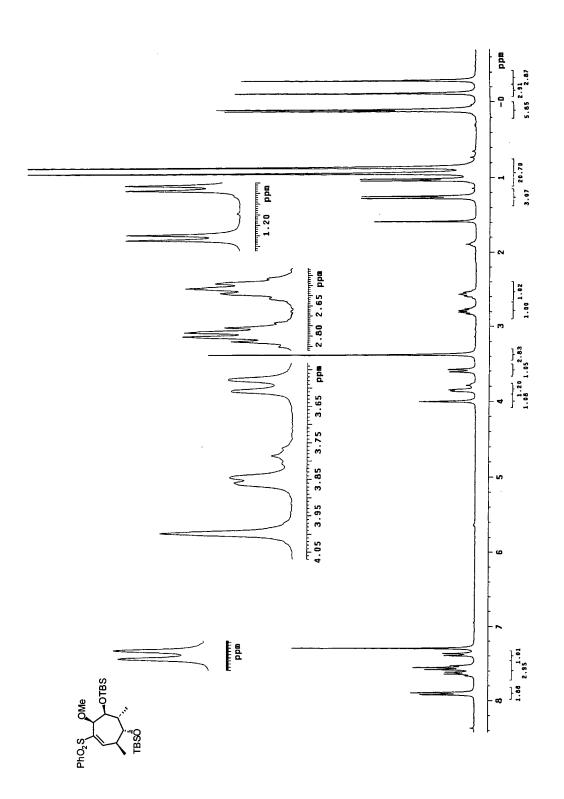
75MHz  $^{13}\mathrm{C}$  NMR of compound 62 in CDCl<sub>3</sub>



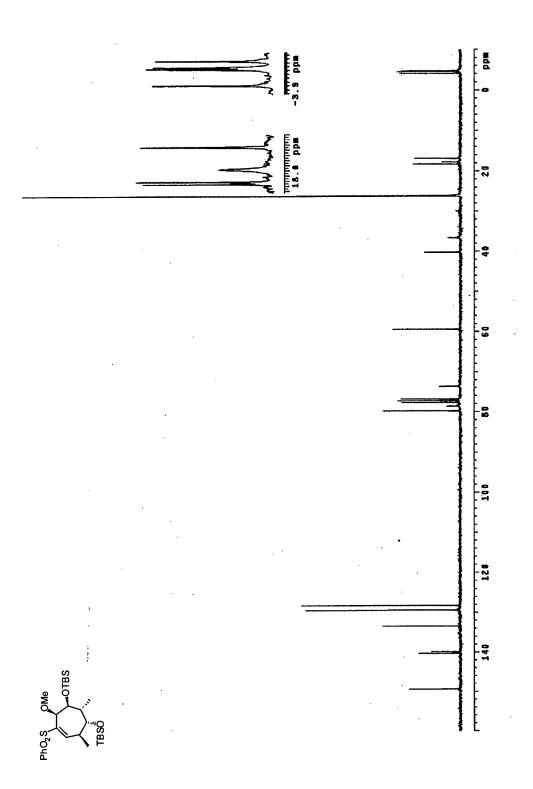
 $300 \mathrm{MHz}\ ^{1}\mathrm{H}\ \mathrm{NMR}$  of compound  $52\ \mathrm{in}\ \mathrm{CDCl_{3}}$ 



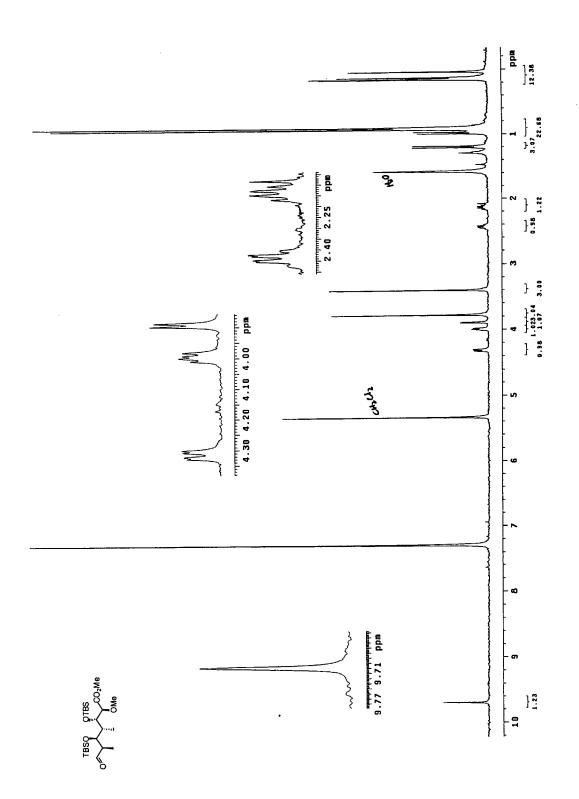
75MHz <sup>13</sup>C NMR of compound 52 in CDCl<sub>3</sub>



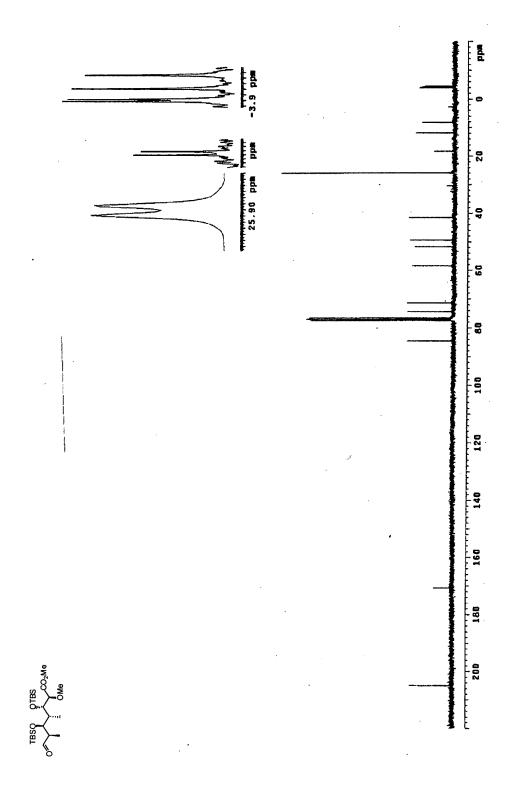
 $300 \mathrm{MHz}\ ^{1}\mathrm{H}\ \mathrm{NMR}$  of compound  $53\ \mathrm{in}\ \mathrm{CDCl_{3}}$ 



75MHz <sup>13</sup>C NMR of compound 53 in CDCl<sub>3</sub>



 $300 \mathrm{MHz}$  <sup>1</sup>H NMR of compound 51 in CDCl<sub>3</sub>



75MHz  $^{13}$ C NMR of compound 51 in CDCl $_3$